

AIR POLLUTANT EMISSIONS, CONCENTRATIONS, AND EXPOSURES FROM
BIOMASS COMBUSTION: THE CIGARETTE ANALOGY

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In recent years, scientific interest in biomass as a fuel has been rekindled, and along with it, concerns over potential environmental effects. This has come about in several ways:

- o In those areas of industrial countries where space heating is important, the use of wood has experienced rapid repopularization. Indeed, in the United States, since the first oil crisis the use of wood for fuel has grown much faster than any other energy source, 7 percent per year since 1973 (1).
- o In many developing countries traditional biomass fuels, which include wood, crop residues, and animal dung, still supply energy needs. Since the energy crisis, international concern has grown about the dual problems of finding more energy for economic development and at the same time preventing the rapid deforestation that has come to accompany too much reliance on local biomass fuels. Efforts to solve these problems have focused on increasing supply through such innovations as fast-growing tree plantations and improving the efficiency of use through such devices as improved stoves. This problem is recognized to be significant since more than half the world's population relies on these traditional biomass fuels for nearly all their energy needs, a situation that has not changed since the discovery of fire.
- o In both developed and developing countries, there is at least one other reason for increased interest in biomass fuels. Partly through reapplication of processes developed and left by the wayside in the past and partly through application of sophisticated new understandings of biomass processing, there are now a range of technologies being examined that basically act to convert simple biomass feedstock into high-quality solid, gaseous, and liquid fuels. These are the fuels that will be needed to hasten economic development in poor countries and to fulfil the biomass portion of the renewable-energy promise in all countries.

With the revitalization of biomass fuels, the citizens of developed countries are discovering what their ancestors knew well and their neighbors in developing countries still experience--in small-scale combustion conditions biomass fuels have significant emission factors for several important air pollutants. As shown in Table 1, the emission factors for three of the five priority pollutants, particulates, hydrocarbons, and carbon monoxide, compare unfavorably with those of coal combustion when the burn rate is in the range of a few kilograms per hour (2-25 kW). At industrial scale (a few hundred kilograms per hour) biomass emission factors do not usually appear so much worse than coal, a conclusion tempered by the significant affect on emissions of the particular combustion conditions and quality of the fuels.

In the last few years, an increased amount of effort has gone into studying the emission characteristics of biomass-fueled (mainly by wood) heating stoves of the types commonly in use in developed countries (2). This is becoming more of a concern as outdoor smoke* levels rise in communities relying on such appliances. In some states of the United States, for example, emissions from wood stoves have exceeded

*Here I will use the term "smoke" to refer to the entire mixture of emissions from biomass combustion: all gases and aerosols.

those from industry for critical pollutants (3). Woodsmoke studies have characterized a large number of organic compounds in the "hydrocarbon" portion of the emissions. Indeed, several hundred have been identified, many of which are polycyclic aromatic hydrocarbons (PAH) that have been shown to be mutagenic or carcinogenic (4).

Although the problem of smokey village kitchens has long been noted by observers in rural areas of developing countries, it has been only recently that systematic indoor measurements have been undertaken (5). The human exposures to several important pollutants that can be estimated as a result of these concentrations are orders of magnitude higher than typical urban exposures.

Unfortunately, just as there have been few and only relatively recent quantitative studies of the concentrations, there are very few quantitative epidemiological studies about the health effects of biomass smoke, although there exists much anecdotal information by medical observers and others. Until this lack is remedied, it is necessary to rely on extrapolations from studies of other situations.

The most obvious extrapolation is from urban epidemiological studies of air pollution. Unfortunately, however, there are severe limitations with respect to extrapolating these studies to biomass smoke. Although many of the same pollutants have been studied, the mix is so different as to make comparisons suspect. Urban particulates, for example, are usually associated with sulfur oxides because of the composition of their principal source--fossil fuels. Consequently, the major official reviews of the health effects of particulates are unable to separate the effects of the two pollutants (6). In air polluted by biomass smoke, however, particulates are usually associated with carbon monoxide and hydrocarbon vapors and droplets. There are further important differences between typical fossil-fuel smoke and biomass smoke in the size distribution and chemical nature of the aerosols, percentage of elemental carbon, content of trace metals, and so on.

There is, however, a form of biomass smoke that has been studied extensively, to an extent rivaling urban air pollution. This is entirely appropriate because this form of biomass smoke is the cause of more human air pollution exposure and greater human ill-health than all other causes of air pollution combined. It is, of course, tobacco smoke.

If an analogy could be drawn between exposures to tobacco smoke and exposures to the smoke from biomass fuels, then investigators of the impact of the latter would have access to a vast health effects literature available for the former. It is the purpose of this paper to begin an exploration of the viability of this analogy.

To effect this comparison, I have chosen to examine four pollutants found in significant amounts in biomass smoke of all kinds: respirable particulates (RSP), carbon monoxide (CO), formaldehyde (HCHO), and particulate benzo(a)pyrene (BaP). Each of these has been the subject of considerable attention in its own right as a health-damaging pollutant. They each also represent an important member of one of the four principal classes of pollutants found in biomass smoke: particulates, gases, hydrocarbons, and PAH. To test this analogy in a quantitative manner, I will separately examine for cigarettes and woodfuel the relative emission factors, air concentrations, and nominal human doses of these four pollutants.

Emission Factors

Researchers of cigarette emissions have had to develop a standard smoking procedure such that different brands can be compared on as much of an equivalent basis as possible. The procedure used in most studies today is to smoke each cigarette in 10 puffs at one-minute intervals with a puff volume of 35 ml and a puff duration of 2 sec. The smoke coming through the mouthpiece of the cigarette that

would normally be respired by the smoker is called the mainstream smoke. The smoke released from all points of the cigarette between puffs is called sidestream smoke. Specialized machines have been developed to "smoke" cigarettes in this fashion and to measure the particulate and gaseous emissions (7).

At present there is no standard procedure for measuring emissions from small cooking or heating stoves although such procedures are under development (3, 8). In order to make quantitative comparisons between cigarette smoke and the smoke from biomass-fueled appliances it will be necessary to choose emission factors from those available in the literature. Since the emissions from enclosed metal heating stoves vary dramatically with stove operating conditions, it would seem appropriate to confine this initial set of comparisons to what seems to be the less variable open combustion conditions typical in fireplaces and simple cooking stoves. Excluding cigarette burning, open combustion of this sort is, after all, the most common combustion situation in the world regardless of fuel type.

Although over 3000 different compounds have been identified in cigarette smoke, a few dozen are singled out as most important. A few of these are shown in Table 2 and include the four being considered in this paper. Note that the tobacco smoke literature calls "tar" what the air pollution literature calls "total suspended particulates (TSP)." The emission factors in the table refer to mainstream smoke and a separate column lists the relative amounts of emissions from sidestream smoke. These emission factors vary by brand, by type of filter, and way of smoking. They also vary by time in that cigarettes in the United States, at least, have lower average emission factors today than they did in past years, and the relative toxicity of the emissions on a mass basis seems to be going down as well (9).

Since the amount of biomass actually burned in a typical cigarette is about one gram, the emission factors in Table 2 that are listed in mg are equivalent to g/kg. The first column of Table 3 compares the emission factors of mainstream and sidestream cigarette smoke with those representative of woodsmoke from small-scale combustion. Note that, except for TSP, the emission factors for wood are similar to or higher than those for tobacco. Note also, that the difference between sidestream and mainstream tobacco smoke is large for many species, indicating HCHO and a number of the gas-phase nitrosamine compounds. For TSP (tar), CO, and BaP, on the other hand, the ratio is much smaller.

Another factor of interest with particulates is their size range. In this respect, as well, cigarette smoke and woodsmoke are similar. Each has a mass median diameter of less than 0.4 μm , indicating that essentially all the particulate matter penetrates into the deep lungs upon respiration (10). In air pollution terminology, essentially all TSP is RSP.

Concentrations

There are two distinct types of cigarette smokers--active and passive (or voluntary and involuntary). The active smoker experiences high concentrations of pollutants because the mainstream smoke is mixed with the relatively small amount of air in a breath, the tidal volume. In the standard cigarette smoking sequence there is one "puff" per minute for ten minutes. Since the sales-weighted cigarette in the United States in 1980 released 14 mg of "tar" per cigarette in the mainstream smoke and the tidal volume of air for an adult woman in light activity is about 940 ml (11), the particulate concentration would be about 1500 mg/m^3 . This is some two or three orders of magnitude higher than the measured average TSP concentrations in air breathed by women cooks in rural field studies in Asia (5).

BaP concentrations in mainstream cigarette smoke, on the other hand, are quite similar to those in village homes, as are HCHO concentrations. CO levels are intermediate. The second column of Table 3 lists the relative concentrations experienced by a village cook and a smoker for these four pollutants.

A passive smoker will experience concentrations that are determined and can be accurately estimated by the number and location of cigarettes being smoked nearby, the room volume, ventilation rate, and mixing conditions. (12). In a well-mixed conference room (200 m³; 2ACH; 40 people half of whom are smokers, each of whom smokes 2 cigarettes per hour), indoor concentrations of the four principal pollutants can be calculated from the sidestream emission factors in the first column of Table 3 and the result is shown in the second column. By this estimate, the passive smoker would experience concentrations of three of the pollutants much lower than the active smoker and consistently lower than the village cook. Note also, that because of the large ratio of sidestream to mainstream emission factors for HCHO (Table 2), the passive smoker can actually experience concentrations of HCHO comparatively similar to those experienced by the smoker. It is important to remember, however, that the smoker "puffs" only once a minute (~ 5 percent of breaths) while the passive smoker and village cook experience these concentrations in every breath during the exposure period. The relative doses, therefore, are not the same as the relative concentrations.

There is a further refinement possible in these concentration estimates. Since the mainstream smoke is not entirely deposited or absorbed by the respiratory system of the smoker, there is an addition to the surrounding indoor air concentrations resulting from the exhaled air of the smokers. (13) Furthermore, of course, that the active smokers in the room with passive smokers will experience at least as high "passive" concentrations in the 95 percent of breaths that are not "puffs" on the cigarette.

Nominal Doses

To understand the relative health effects of pollutants it is always best to measure dose, the actual amount of material absorbed or deposited in the body. There is variability, however, in the way air contaminants are deposited or absorbed by different people at different times. The breathing rate, whether mouth or nose breathing is occurring, and the condition of the respiratory system all affect deposition, for example. In cigarette smokers, there are the additional variables of smoking behavior. If the smoker inhales the smoke and smokes the butt down to almost nothing, the dose per cigarette is going to be much larger than that of a normal smoker.

In addition, although woodsmoke and tobacco smoke have many similarities, there are also differences. The temperature of cigarette smoke, for example, would normally be higher. There may be some sort of saturation effect at the generally higher concentrations experienced by the active smoker leading to lower deposition rates per gram of material inhaled. On the other hand, the hot dense smoke from smoking may inhibit or damage natural lung clearance and other defense mechanisms to the extent that deposition efficiency is higher with such exposures. It may be, however, that the 95 percent of breaths that are low exposure for the active smoker allow the lung defense mechanisms to operate more efficiently than they can when every breath contains significant concentrations.

Not knowing the deposition or absorption rates with accuracy means that it is not possible to calculate exact doses. For the purposes here, it is sufficient to address what has been called "nominal dose" (12), here being defined as the amount of material actually breathed in by the smoker or cook. I will assume linearity in response to exposures and correct for breathing rates and particle sizes. The reference woman in (13) breathes 18.2 m³ of air during 16 hours of light activity and 2.3 m³ during sleep per day and about 95 percent of the particles are respirable (10). Consequently, the comparative daily exposures of the four major pollutants for a two-pack-per-day smoker and a village cook are as shown in the last column of Table 3. The village cook receives nominal doses of BaP and HCHO that are higher than those received by the smoker by factors of 12 and 2.8 respectively. The smoker, on the other hand, receives nominal doses of CO and TSP that are greater by factors of 4 and 24.

Using the same assumptions as those used to calculate concentrations in Table 3, and assuming a 4-hour meeting in the conference room, the passive smoker would receive daily nominal doses lower than either the active smoker or the village cook. This assumes, of course, that this person is exposed to no other conditions of poor air quality during the day. Note that the exposure to HCHO is much closer to that of the active smoker than are the relative exposures of the other species. This is because of the large emissions of HCHO in sidestream as compared to mainstream cigarette smoke. Indeed, the HCHO exposure rate per hour during the conference meeting for the passive smoker is nearly three times that of the mainstream exposure rate received by the smoker in smoking two cigarettes per hour. This means that the total HCHO nominal dose of the active smoker at such a meeting is mostly due to her role as passive rather than active smoker.

In Table 3, the Upland Sleeper is someone who lives in a highland area such as those in Nepal, Peru, Kenya, and Papua New Guinea. She is presumed to spend 14 hours a day in the house during which she sleeps for 8. If one assumes that the average exposure during this period is about 50 percent of that received by the cook near the fire, the upland sleeper would receive a total daily nominal dose of each pollutant roughly 40 percent greater than the cook.

Of course, active smokers also receive passive exposures if they attend conference meetings with smokers present and village cooks in upland areas also must sleep. To a first approximation, the total daily nominal dose for women in these situations would be the total of the active and passive smokers' nominal doses and the total of the cooking and sleeping nominal doses respectively. Further corrections could be made to account for any ambient exposures received by these groups.

Conclusion

Of the four pollutants examined here it seems that nominal doses to two of them are roughly similar for cigarette smokers and village cooks--HCHO and CO. For RSP, active smokers receive more than a factor of 10 larger nominal doses. On the other hand, village cooks receive more than a factor of ten greater nominal doses to BaP. In all cases, village cooks receive higher nominal doses than passive smokers. On the basis of these comparisons, therefore, it might be expected that the health impacts among village cooks would lie somewhere below those for active smokers and well above those for passive smokers. It should be mentioned, however, that many other pollutants are not addressed here. Nicotine, in particular, would seem to be something nearly absent in woodsmoke and yet an important health-damaging pollutant in tobacco smoke. Nevertheless, even a rough index such as the one here is suggestive. There has long been evidence that smokers harm themselves (9, 14) and there is a rapidly growing consensus that passive smokers' health is also affected (15). The index could also be expanded to characterize the particulate fraction by chemical (16) or bioassay (17) techniques or a combination (18).

The data in Table 3 can also be used for other comparisons. Consider the relative emissions of a coal-fueled electric power plant and a cigarette. In 1981, the average U.S. resident was responsible for the burning of about 3.5 kg of tobacco and 2900 kg of coal, 82 percent of which was used in power plants (19). In a study at Brookhaven National Lab, it was determined that a typical coal power plant delivers about 0.1 mg-person-year/m³ of exposure for every ton of particulate emissions (20). Assuming that all the coal power plants emit particulates at the legal limit implies that the coal-derived electricity needs of the average U.S. citizen cause about 0.003 mg-person-year/m³ of exposure. Using the data and assumptions in Table 3, it can be shown that typical wood needs for cooking in a developing country (about 400 kg/capita-year) would produce about 0.15 mg-person-year/m³ or 40 times the exposure caused by six times more fuel in the U.S. power plants. Even more strikingly, it can be estimated that compared to the coal

used per capita the tobacco needs of the average U.S. citizen causes about four orders of magnitude more exposure simply to the passive smokers nearby and not even counting the much larger exposures to the smokers themselves.

The lesson should be clear. When the objective is to protect human health, it can be quite misleading to concentrate solely on emission factors and total emissions. Distributed combustion sources, such as cook stoves and, in the extreme, cigarettes, can be responsible for much larger human exposures per unit fuel. This fact has important implications for the design of alternative energy systems. (21)

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Table 1. Comparison of Air Pollutant Emission from Energy-Equivalent Fuels
(in kilograms)

Fuel (Efficiency)	Fuel Equivalent to One Million Megajoules Delivered	Particulates	Sulfur Oxides	Nitrogen Oxides	Hydro- carbons	Carbon Monoxide
Industrial						
Wood (70 %)	80 metric tons	480	56	360	360	400
Coal (80 %)	43 metric tons	2,080	810	1,180	6	45
Residual oil (80 %)	33,000 liters	94	1,310	240	4	20
Distillate oil (90 %)	31,400 liters	8	1,120	83	4	19
Natural gas (90 %)	28,200 cubic meters	7	neg.	99	2	8
Residential						
Wood (40 %)	144 metric tons	2,170	86	110	1,450	18,790
Coal (50 %)	69 metric tons	520	1,200	270	430	2,380
Distillate oil (85 %)	32,900 liters	11	1,170	71	4	20
Natural gas (85 %)	30,000 cubic meters	7	neg.	38	4	10

Source: 22.

NOTE: These are typical but not average figures. Actual efficiencies and emissions depend on fuel quality and combustion conditions. Residential heating stoves under US conditions.

Table 2: Major toxic and carcinogenic species in cigarette smoke; ratio of sidestream smoke (SS) to mainstream smoke (MS)

A. Gas phase	Amount/cigarette		SS/MS
Carbon dioxide	45	mg	8.1
Carbon monoxide	13.25	mg	2.5
Nitrogen oxides (NO _x)	308	µg	5.25
Ammonia	70	µg	58.50
Hydrogen cyanide	415	µg	.27
Hydrazine	32	µg	3
Formaldehyde	55	µg	51
Acetone	520	µg	2.85
Acrolein	75	µg	12
Acetonitrile	110	µg	10
Pyridine	32	µg	10
3-Vinylpyridine	23	µg	28
N-Nitrosodimethylamine	92	ng	420
N-Nitrosoethylmethylamine	20.5	ng	17
N-Nitrosodiethylamine	14.05	ng	14.5
B. Particulate phase	Amount/cigarette		SS/MS
Total particulate phase (tar)	14	mg	1.6
Nicotine	1.18	mg	2.95
Toluene	108	µg	5.6
Phenol	85	µg	2.6
Catechol	160	µg	0.7
Naphthalene	2.8	µg	16
2-Methylnaphthalene	1.0	µg	29
Phenanthrene	41	ng	2.1
Benz(a)anthracene	40	ng	2.7
Pyrene	52.5	ng	2.75
Benzo(a)pyrene	24	ng	3.05
Quinoline	1.7	µg	11
Methylquinoline	6.7	µg	11
Harmane	2.1	µg	1.7
Norharmane	5.65	µg	2.85
Aniline	650	ng	30
o-Toluidine	32	ng	19
2-Naphthylamine	15.65	ng	39
4-Aminobiphenyl	3.5	ng	31
N-Nitrosornicotine	1.95	µg	3
N-Nitrosoanatabine	2.38	µg	4

Source: 14.

Table 3: Summary of Emission Factors, Concentration, and Nominal Doses of Tobacco and Woodsmoke

	Active Smoker	Passive Smoker	Village Cook	Upland Sleeper
Emission Factors (per kg of biomass)				
CO	17 g	43 g	40 g	40 g
TSP	14 g	24 g	2.0 g	2.0 g
BaP	0.03 mg	0.1 mg	1.0 mg	1.0 mg
HCHO	0.03 g	1.5 g	0.4 g	0.4 g
Concentration (per cubic meter of air)				
CO	1800 mg	5.2 mg	50 mg	25 mg
TSP	1500 mg	3.1 mg	7 mg	3.5 mg
BaP	3100 ng	13 ng	4000 ng	2000 ng
HCHO	3.1 mg	0.15 mg	1.0 mg	1.0 mg
Nominal Dose (per day)				
CO	680 mg	23 mg	170 mg	240 mg
RSP	530 mg	13 mg	22 mg	32 mg
BaP	1100 ng	54 ng	13,000 ng	18,000 ng
HCHO	1.2 mg	0.66 mg	3.3 mg	9.7 mg
Assumptions				
TSP and BaP	940 ml/breath	200 m ³ room	Measurements	50% cook
95% respirable	10 puffs/cig.	40 cig./h.	in India,	concentrations
Adult women	2 packs/day	2 ACH	Guatemala, and	14 hours indoors
		perfect mixing	New Guinea	9.7 m ³ total air
		4-hour meeting	1.1 m ³ /h	
		1.1 m ³ /h		

NOTES:

A cigarette smoker in the same 4-hour meeting as the passive smoker would receive a total nominal dose equivalent to approximately the two added together. Similarly, a village cook living in an upland area would receive a nominal dose roughly equal to the two added together.

If the smoker is assumed to exhale half of the respired pollutants, the passive smoker's concentrations and doses could be expected to be larger by CO: 20%; TSP: 30%; BaP: 15%; HCHO: 1%.

Source: 14, 11, 5, 23, 24, 8.

EMISSION FACTORS AND EFFICIENCIES
FOR SMALL-SCALE OPEN BIOMASS COMBUSTION:
TOWARD STANDARD MEASUREMENT TECHNIQUES

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Introduction

A large fraction of the population of the earth is served by the preparation of food and space heating by small fires. In many cases the cooking is done indoors and the combustion products are not vented out of the building, but simply escape through windows, doors, and porous walls and roofing. This report describes a preliminary step in defining a test protocol for the simultaneous measurement of efficiency and emissions of open biomass cooking/heating stoves as they are used in many developing countries. This study is part of a larger study of the health impacts of these combustion sources [Smith and others (1)].

Previous studies of total suspended particulates by Smith et al.(2), and carbon monoxide concentrations in village houses by Dary et al.(3) show that exposures are significant and may approach or even exceed those experienced by cigarette smokers (4). Another aspect of biomass fuel use which is of considerable importance in some areas is the availability of fuel and ways in which the efficiency of fuel use might be increased [de Montelembert and Clement (5)].

There have been many studies of efficiencies and emissions for metal wood-fired spaceheaters [Cooper & Malek, (6)] and there have also been several studies of the efficiencies of fuel use for undeveloped countries [Prasad (7)]. The test protocol described here attempts to combine two important objectives:

- 1) The burn conditions in the tests should simulate as closely as possible those expected in the field;
- 2) The testing should combine efficiency and emission measurements.

The combustion region in a village house is defined by the stove, which confines the fire and supports the cooking utensil, and also by the cooking utensil itself. An important benefit of combining efficiency and emissions tests is that future work on the design of improved stoves can evaluate changes and potential compromises between emissions and efficiency goals.

Another objective of this study is the design of a measurement system that could be replicated at a reasonably low cost and operated by individuals with limited experience with emissions and efficiency testing. Such easily assembled systems might then be made available at field locations in the relevant countries, where local institutions familiar with local customs and fuel types could examine ways of improving the performance of the combustion systems. While perhaps not satisfying the requirements for accuracy necessary for showing compliance to regulatory requirements, such a system could be very useful for designing and testing improved stove/fuel combinations.

Apparatus and Materials

The tests were conducted in a small (17m³) utility building of the type often

used for equipment storage. The building had a concrete floor, a sliding entrance door, and sliding windows on two sides. This building was also used to stimulate a village hut (8). The cookfire was built in a stove in the corner of the building and the emissions were collected by a hood that is a quarter section of a cone and could be raised and lowered over the fire. The hood fitted into a corner of the building. Air in the hood was exhausted from the building at a rate of about 10 m³/min through a 0.2 m diameter duct with a 1/3 hp blower located just outside.

Such an arrangement is quite different from those typically used to measure emissions from the types of woodfired stoves in common use in industrial countries (6). Such stoves have flues and emissions measurements can be made by insertion of probes into the flue-gas stream. The stoves of interest here, which are the most common stoves in the world, have no flues. The emissions testing equipment must capture all the emissions without significantly altering the combustion characteristics of the stove.

The movable hood met these specifications in our tests. The hood was raised to about 0.6 m in order to change stoves and clean up after tests. Most types of simple biomass-fueled cookstoves (8,9) without flues could be placed or constructed on the floor under this hood. The hood was then lowered to about 0.3 m. This allowed all the emissions from the fire to be captured by the hood exhaust, but is not so close to the stove that it creates a greatly increased air flow through the combustion region.

TSP and CO were sampled just upstream of the blower. The air flowrate through the exhaust duct was inferred from the pressure drop across an orifice plate in a section of 0.15 m diameter duct downstream of the blower. The flowrate was calibrated to the pressure drop by making an absolute measurement of the flowrate with a pitot transverse in a straight section of the duct downstream from the orifice plate. The calibration was performed on two occasions. Although the blower capacity was degraded somewhat by the buildup of particles on the blower vanes, the orifice calibration was not significantly affected. The air was exhausted at a location about three meters from the building. The entrainment of the exhaust gases was not a problem during these experiments.

Stainless steel and copper probes (1/4" I.D.) facing into the air flow removed aliquots of the total emissions. These were passed through filter cassettes (for TSP) or through a damping volume and then taken through an Ecolyzer CO monitor (Model 2100; modified to a detection range of 0-500 ppm). The CO stream was drawn by the pump in the Ecolyzer which operated at about 1.2 liter/min. The Ecolyzer was calibrated with a 203 ppm CO standard (span gas). The sensitivity of the instrument was such that the measurement error of the CO concentration ranged from 4 to 8 ppm.

The particulate matter sample stream was drawn by a battery powered personal sampler (Gilian model HFS113) at rates ranging from 1.5 to 4 liter/min. The personal sampler was operated in the constant flowrate mode and this rate was monitored by the rotameter on the sampler. The rotameters were calibrated by volume displacement. Several types of 37mm filters were used depending on the desired end-point (glass fiber for TSP, Teflon for TSP and trace metals, quartz for elemental carbon determination).

The temperature in the duct at the sampling probes was generally 30-40° C. The collection method is more similar to that used by Butcher and Ellenbecker (10) in a study of residential heaters than it is to EPA Method 5, which has been used to study emissions from a wide range of combustion sources, including residential heaters (11).

Biomass fuels for these tests should be chosen to represent those in common use in developing countries, which are mainly in tropical areas. Anecdotal accounts by villagers (2) and measurements of emissions from wood species from temperate climates indicate that emissions vary by tree species (6,12). Emissions from various kinds of crop residues vary even more significantly because of greatly varying ash contents and physical characteristics (1). Emissions from animal dung also vary somewhat according to the content of dirt incorporated during the collection process. The emissions from all biomass fuels can be expected to vary by moisture content.

In these preliminary tests, six tropical tree species, cow dung, coconut husks, and charcoal were used. Collection, drying, and storage procedures were designed to result in a range of moisture contents typical of what would be expected in the field.

Test Procedure

The heat utilization measurements were based on the provisional international standards developed by Volunteers for International Technical Assistance (13). The temperature of two liters of tap water was determined and then placed in a covered cooking pot. The fire was started under the pot with the aid of a small measured amount of kerosene to help insure that each test began in a consistent manner. The particulate samplers were started as the fire was lit. The fire was actively tended by adding fuel, rearranging fuel, and blowing on the fire through a blowpipe, as needed. Fires in real field situations usually receive similar attention. A fairly vigorous fire was maintained to raise the water to the boiling point and to boil it for 15 minutes. When the water boiled, the time was noted. After boiling for 15 minutes the fire was reduced to keep the water at a simmer ($>95^{\circ}$) for 30 minutes. At the end of this period the fire was extinguished and the samplers were turned off.

The amount of fuel added and the fuel residue were determined by a pan balance to an accuracy of 1g. Charcoal and unpyrolyzed wood residues were weighed separately. The amount of kerosene added was recorded and the amount of water remaining in the pot was determined.

Two types of "efficiency" of the cooking process were determined. The first was the "overall heat utilization," which is the ratio of the heat output (sensible + latent heat of the water) to the heat input in terms of the heats of combustion of fuels used (the "low heat value," corrected for moisture content and charcoal residues). The kerosene used for lighting accounted for only a small fraction of energy used. The second was the "net heat utilization" and is the ratio of sensible heat output to heat input. Both measures of heat utilization are useful, depending on the type of cooking being considered. A third "power" measure is sometimes important as well: it is the average stove power during the heat-to-boil phase of the test cycle. This was not determined in these tests because the power test required stopping the fire to weigh the fuel. Starting and stopping the fire, unfortunately, greatly affects emissions. Joint power and emissions tests would require some other technique, perhaps placement of the entire stove on a large scale.

During the burn, the air sampling equipment was monitored more or less continuously and critical values were recorded at 5-minute intervals. These values included orifice-plate pressure drop, sampler flow rates, duct temperature at the sample probes, ambient temperature, and Ecolyzer reading.

The filters were placed in a dessicator for 24 hours before the tare and

sampled weights were taken. Weights were then measured to within 0.01 mg. In most cases, each filter represented an integrated sample over the entire burn. The total particle emissions were determined as the product of the filtered weight and the ratio of the total duct flow to the particle sampler flow. The emission factor for particulate matter was then calculated as the ratio of total particle emissions to net fuel consumed. These particulates could be expected to have mass median aerodynamic diameters of about 0.6 μm or less based on wood and dung smoke measurements in open and closed stoves (8,14). This means that essentially all TSP is within the respirable range ($<2.5 \mu\text{m}$).

The carbon monoxide concentration in the duct was obtained from the Ecolyzer reading (corrected for temperature). The duct concentration was then integrated over the time of the burn and multiplied by the flow rate through the duct to obtain the total carbon monoxide emissions. The emission factor was obtained by dividing by the fuel consumed, as described above.

Results and Discussion

The results of seventeen test burns are summarized in Table 1. These results are sorted by stove type. The chulas were constructed of firebrick or of large stones. The conventional chula is U-shaped and open at the top to support the cooking utensil. It is constructed of clay or similar indigenous materials. The C.P.R.I. stove is a cylindrical metal stove designed for increased heating efficiency. The fuel use rate ranged from 0.2-1.6 kg/hr. A number of different fuels were tested, but these results are aggregated for present purposes. The large variations in emissions factors very likely resulted from variations in the burning conditions from one burn to the next and also from errors of measurement. Variations in the burning conditions occur naturally and have also been observed in other stove tests (8,10). These variations can only be minimized by conducting many tests. Key among the measurement errors are those which arise from weighing the 37 mm filters. For some cases the particulate weight was less than 0.10 mg and near the limit of sensitivity of the available balance. There may also be problems associated with the adsorption of gases such as SO_2 on glass fiber filters.

Other problems may arise from the configuration of the duct near the sampling probes. The sampling probes were located fairly close to a right angle bend in the ductwork and just upstream of the blower inlet. Substantial inhomogeneity of the flow field was observed in this region and the particle collection efficiency may have depended on the sample probe location and orientation. Particle losses in the duct upstream of the sampler were estimated by measuring the deposition on weighed aluminum foil. For a series of burns in which the total emissions were 62 grams, about 5 grams were estimated to have been deposited in the duct.

The emissions factors in Table 1 may be compared with factors obtained by others for fireplaces. Fireplaces, although usually not tended continuously like chulas, are more similar to chulas than are closed metal stoves. Dasch (14), in a fireplace study using EPA Method 5, obtained an average of 5.4 g/kg for filterable particulates with a range of 2.4-12 g/kg. The condensible organic fraction averaged 6.9 g/kg with a range of 2.3-22 g/kg. DeAngelis, et al. (11), obtained averages of 2.4 g/kg particulates and 6.7 g/kg condensible organics for fireplaces. The results obtained here tend to fall between values for particulates only, and those for particulates plus condensibles from these other studies. Further work is needed to define the sampling method most appropriate for assessing the health effects of these low temperature combustion sources.

Dasch (15,16), Lips (17), and DeAngelis, et al. (11,18) obtained average carbon

monoxide emission factors which ranged from 16 to 110 g/kg in fireplace studies. This range includes several burns carried out at much higher combustion rates than we have used. Smith, *et al.* (8), in a study of concentrations in a simulated village hut which allowed the determination of emission factors by indirect means obtained the results at the low end of the range. Additional research is being conducted to explain this discrepancy.

Table 1
Summary of Results
Mean Values (range)

Stove	Overall Efficiency	Particle Emission Factor	Carbon Monoxide Emission Factor
Small Chula 9 burns	13.3% (9.0-16.6)	9.1 g/kg (4.2-21.3)	84 g/kg (72-92)
Large Chula 2 burns	14.2	12.3 (9.1-15.5)	~88 (76->101)
Three Rock Chula 3 burns	11.6 (6.7-14.3)	7.7 (4.2-10.2)	63 (39-81)
C.P.R.I. Stove 3 burns	15.5 (11.8-18.0)	5.2 (0.3-8.3)	182 (86-360)

The current system using personal samplers offers the advantage of simple and stable pumps usable in other applications such as personal sampling. A disadvantage is that the small sample volumes result in particle masses than can only be determined with a sub-milligram level analytical balance. In many cases the filtered masses of 1-5 mg were easily measured, but for some fuels these masses were less than 0.1 mg. The advantages of using the present system will be compared with those using a large volume of air and less demanding weighing procedure in future work.

Some aspects of the sampling method are bound to affect the operation of the fire somewhat and one can only try to minimize these effects. As mentioned, the 0.3 m distance from the hood to the floor means that the hood opening is about 0.54 m² for these studies. At an average flowrate of 10 m³/min, this gives an average face velocity of about 19 m/min. It is difficult to say how much of an effect this airflow has on the fire. We do know that fugitive emissions to the interior of the hut was a minor factor for these tests. Generally speaking, very little smoke was apparent in the hut. The CO concentration was measured at the edge of the hood on three occasions. Two of these measurements were less than the detection limit of the system as set up (less than 2 ppm), and one measurement was about 4 ppm.

Although there are several remaining problems to be solved in this system, it seems that it can be useful as an inexpensive approach to measuring thermal efficiency and air emissions from simple open biomass-fired stoves.

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PARTICULATE EMISSIONS FROM LOW GRADE FUEL HANDLING. Joseph M. Sorge and
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The harvesting storage and handling of low grade carbonaceous fuel may result in significant particulate emissions if proper mitigation measures are not observed. The paper provides a summary of particulate size distribution data available for peat and biomass fuel processes. Using the size distribution data and EPA transportation emission rates an estimate of dust emissions from a moderate facilities is developed. Several alternative dust control strategies are assessed to determine respective cost and feasibility information. Results are developed for selective climatic regions to project the severity of the dust emission problems in typical areas of the U.S. The results obtained indicated that the use of practical mitigation methods can substantially reduce the impact of dust emissions due to low-grade fuel harvesting, storage and handling processes.

COMPARISON OF ATMOSPHERIC ENVIRONMENTAL INTRUSIONS OF VARIOUS POWER PLANTS

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INTRODUCTION

The conversion of coal into useful products by combustion or gasification results in the emission of waste materials that are undesirable additions to the environment. These emissions must be controlled in order to prevent damage to the environment, its inhabitants, and their possessions, and to comply with regulations. The objective of this environmental analysis is to assess and compare the environmental intrusions into the atmosphere of conventional coal-fired electric utility plants burning pulverized coal (PC), pressurized fluidized bed combustion power plants (PFBC), coal gasification combined cycle power plants (CGCC), magnetohydrodynamic power plants (MHD), and molten carbonate fuel cell power plants (MCFC). The plants are ranked according to their rates and amounts of emissions.

EMISSIONS

The combustion of coal or of coal-derived fuel gases results in the production and emission into the atmosphere of particulates, sulfur oxides (SO_x) nitrogen oxides (NO_x) and carbon oxides (CO_x). These are derived from the mineral matter in the coal, mineral and organic sulfur in the coal, and organic nitrogen in the coal, producing fuel NO_x . Additionally, the high combustion temperatures result in thermal NO_x being formed from nitrogen in the combustion air.

The particulate matter emitted when coal is converted consists primarily of ash derived from the mineral matter of the coal, mixed with some unburned coal, plus elutriated bed material, if any. In the event that the temperature of the flue gas drops below about 300°F , depending on sulfur content of the fuel, droplets of sulfuric acid may condense, giving rise to an acid aerosol or mist.

Coal sulfur is converted to oxides, SO_x , during combustion, or to H_2S during gasification. From combustion, over 95% is in the form of SO_2 , with less than 5% as SO_3 , as emitted. Although SO_2 is considered harmful to health and welfare, SO_3 is even more so. After emission, the SO_2 is slowly converted to SO_3 . The SO_3 combines with water vapor to form sulfuric acid mist or rain and with basic compounds to form sulfates. Emitted H_2S will also be oxidized to SO_3 . Gasification also results in the formation of small amounts of COS and even smaller amounts of CS_2 .

The nitrogen oxides NO and NO_2 are collectively called NO_x . NO_x is formed from nitrogen both in the fuel and in the combustion air. The percentage of fuel N_2 converted to NO_x

decreases as the percentage of fuel-bound nitrogen increases but the absolute amount converted increases, since the percentage conversion decreases less rapidly than the percentage contained increases. Sunlight converts the emitted NO_x , which is about 90 to 95% NO , into NO_2 , which is unhealthy and contributes to acid rain by forming nitric acid. In addition to the NO_x from fuel discussed above, NO_x is also produced from the nitrogen in the combustion air. This is called thermal NO_x . The amount of thermal NO_x produced is a function of combustion temperature, combustion air ratio and dwell time.

The nitrogen-containing emissions from gasifiers arise only from the fuel nitrogen, since no thermal NO_x arises under the reducing conditions prevailing. The nitrogen-containing emissions are not NO_x but rather, ammonia, NH_3 , and a trace of hydrogen cyanide, HCN . When the raw fuel gas is burned, the nitrogen compounds will convert nearly quantitatively to NO_x and thermal NO_x will also be formed. This can easily result in excessive final NO_x emissions. If the raw fuel gas is cleaned of ammonia, then final NO_x emissions will be reduced but not eliminated, since thermal NO_x will still be formed.

As an indication of the amounts of these emissions, a typical uncontrolled 1000 MW boiler burning coal containing 3.5% sulfur and 12% ash will emit around 900 tpd of ash, 600 tpd of SO_x , 100 tpd of NO_x , and 28,000 tpd of CO_2 .

POWER PLANT EMISSIONS

The power plants considered in this task are so different in detail that any discussion must either be very general and thus superficial or very detailed and thus bewildering. An attempt will be made to steer between these obstacles. In general, an effort will be made to pick up the raw gases downstream of the primary energy converter in each power plant and to briefly describe how the gases will be brought into compliance with the emission limits given below.

The various power plants were nominally designed for 500 MWe output. Illinois No. 6 coal was used, of 3.5% sulfur and 12% ash, with a higher heating value of 11,500 Btu/lb. However, each design used a particular coal analysis which varied somewhat from these figures. The various outputs and efficiencies are shown in Table 1, where columns 3 and 4 show the usual net figures. Pollutant emissions, though, come from the gross input, so gross figures are also shown in columns 2 and 5.

The pollutants in the raw gases emerging from the coal converters in the various power plants are summarized in Table 2. These data have been collected and derived from various sources¹⁻⁶ as well as internal studies and computer simulations. They thus are indicative rather than representative and should be used for comparison only, not for design purposes. As the raw gases proceed through other portions of the power plants, their compositions can be expected to change. In general, the changes

TABLE 1
COAL CONVERSION PLANTS

PLANT	MWE		EFFICIENCY (%)	
	GROSS	NET	NET	GROSS
PC	546	503	34.96	38.04
PFBC	513	497	39.75	41.01
CGCC	531	502	37.34	39.53
MCFC	533	460	49.94	57.74
MHD	624	504	40.49	51.79

TABLE 2
EMISSION RATES FROM COAL CONVERTORS
(LB/10⁶ BTU)

PLANT	PARTICULATE		SO _x		NO _x		CO ₂
	U ^A	C	U	C	U	C	U
PC	8.6	0.03	4.9	0.6	0.6	0.6	203
PFBC	14.7	0.03	0.6	0.6	0.3	0.2	206
CGCC	5.1	0.03	4.9 _B	0.6	-0 _C	0.2 _D	203
MCFC	1.5	-0	4.9 _B	-0	0.6 _C	-0	203
MHD	20.2	0.03	-0	-0	0.6	0.6	214
EMISSION LIMIT	0.03		0.6		0.6		

A U = UNCONTROLLED, C = CONTROLLED

B SO_x EQUIVALENT IF ALL H₂S AND COS ARE CONVERTED TO SO_x

C NO_x EQUIVALENT IF ALL NH₃ IS CONVERTED TO NO_x

D THERMAL NO_x

are minor in heat removal or recovery sections but are major in gas cleanup sections. Combustion of fuel gases will increase the NO_x content due to thermal fixation of nitrogen in the combustion air.

Also shown in Table 2 are the emissions to the atmosphere after control measures have been applied to the raw gases. In general, the controls have been designed to comply with the EPA New Source Performance Standard (NSPS) for electric utility steam generating units. Strictly speaking, this NSPS applies only to the pulverized coal (PC) and pressurized fluidized bed (PFBC) plants, but has also been used for the other plants in the absence of regulations for them. The exception is the molten carbonate fuel cell plant in which the requirements are set by the fuel cell. There is currently no emission limit for CO_2 from any plant, so no CO_2 control equipment is required.

PULVERIZED COAL POWER PLANT

A conventional pulverized coal-burning boiler raising steam for a turbine to generate electricity is considered, as shown in Figure 1. Figure 2 is a block diagram of the air pollution control equipment selected for this plant.

Particulates

The uncontrolled fly ash emission of $8.6 \text{ lb}/10^6 \text{ Btu}$ will be reduced to the compliance limit of $0.03 \text{ lb}/10^6 \text{ Btu}$ by a combination of an electrostatic precipitator (ESP) and a wet scrubber. The ESP has a specific collection area (SCA) of $200 \text{ sq. ft. per } 10^3 \text{ acfm}$. Its pressure drop is negligible.

Sulfur Oxides

The main task of the scrubber is not particulate removal but rather sulfur oxides removal. The theoretical SO_x emission is $5.2 \text{ lb}/10^6 \text{ Btu}$ but since five percent is assumed to be retained by the ash, $4.9 \text{ lb}/10^6 \text{ Btu}$ emerges. This must be reduced to 0.6 by means of a limestone flue gas desulfurization system employing a spray tower at a liquid-to-gas ratio (L/G) of $200 \text{ gpm per } 10^3 \text{ acfm}$ at a ΔP of 0.5 psi .

Nitrogen Oxides

A typical PC furnace will just about meet the NO_x emission limit. Use of retrofit low- NO_x burners in an existing installation or use of two stage combustion or low- NO_x burners in a new installation will insure compliance.

PRESSURIZED FLUIDIZED BED COMBUSTION POWER PLANT

A pressurized fluidized bed combustion power plant (Figure 3) has a steam cooled PFBC raising steam for electricity generation and providing hot gas for driving a gas turbine which compresses the

PFBC air and also generates electricity. A block diagram of the air pollution control equipment is shown in Figure 4.

Particulates

The particulate load from a PFBC is high due to carry over of ash in the feed coal, plus unburned coal, plus elutriated bed material. A series of high efficiency, high temperature cyclones reduces the loading to a low enough level to protect the gas turbine. However, this level, approximately $0.4 \text{ lb}/10^6 \text{ Btu}$ is still above the emission limit, so that a bag house is used to clean the cooled gas to compliance level. The total ΔP is 7 psi. Advanced design cyclones may be able to meet the emission limit, eliminating the bag house, but probably at an increased pressure drop.

Sulfur Oxides

The dolomite fed to the PFBC at a Ca/S mole ratio of 2.3 is calcined to the oxides. The calcium oxide reacts with the sulfur dioxide formed from the sulfur in the coal to produce calcium sulfate. The magnesium oxide does not react but improves the porosity and hence the reactivity and utilization of the calcine. Thus, the raw gas has a low enough SO_x content to be in compliance, but at the cost of having an increased particulate loading.

Nitrogen Oxides

The low combustion temperature in a PFBC retards the formation of thermal NO_x . Pressurized operation results in lower NO_x formation than does atmospheric operation. There is evidence that any NO_x formed is partially decomposed by reactions with sulfur dioxide and/or calcium sulfate. The net result is that NO_x emissions from a PFBC are below the emission limit, so that no additional control method is needed.

GASIFICATION COMBINED CYCLE POWER PLANTS

Another different system is shown in Figure 5, with the air pollution control equipment shown in Figure 6. Here, an air blown coal gasifier supplies the fuel gas for a gas turbine whose exhaust raises steam.

Particulates

A venturi scrubber at an L/G of 20 and a ΔP of 15 psi is used to remove the bulk of the particles from the fuel gas. Final removal occurs in the Stretford plant.

Sulfur Oxides

The sulfur in the coal appears principally as hydrogen sulfide in the fuel gas. This is removed as elemental sulfur by the Stretford unit for disposal or sale. Residual sulfur content,

nearly all as carbonyl sulfide, is converted to sulfur dioxide in the gas turbine combustor but its emission is low enough to be in compliance with the regulations.

Nitrogen Oxides

The low pressure Combustion Engineering gasifier selected produces no ammonia from the coal nitrogen, so that the only NO_x released is that formed thermally in the gas turbine combustor. Conventional gas turbine control methods will assure compliance.

FUEL CELL POWER PLANT

This power plant, shown in Figures 7 and 8, is the most complicated one considered. It has three sources of electricity: fuel cells, a gas turbine, and steam turbines. The sensible heat in the gasifier fuel gas is used to raise steam, as is that in the gas turbine exhaust gas and the fuel cell effluent gas. The fuel cell effluent gas also drives the gas turbine. Finally, the chemical energy in the fuel gas drives the fuel cells.

Fuel cell gas cleanliness requirements are set by the fuel cells, not by emission standards, particularly for sulfur compounds, which must be reduced to 1 ppm. Particulate and ammonia are much less troublesome.

Particulates

A venturi scrubber with an L/G of 40 and a ΔP of 15 psi is used to remove particulate matter to a level sufficient to meet fuel cell requirements and thus emission standards.

Sulfur Oxides

The Texaco gasifier selected emits principally hydrogen sulfide, which is easily removed to the desired ppm level, but the carbonyl sulfide is not. Therefore, a hydrolyzer unit is used to convert the carbonyl sulfide to hydrogen sulfide. A Selexol unit is used to separate the hydrogen sulfide from the fuel gas. Claus-Beavon units are used to recover elemental sulfur and prevent sulfur emissions to the atmosphere in violation of applicable regulations. Final hydrogen sulfide removal is accomplished with a throw away bed of zinc oxide which adds another ΔP of 10 psi for a total ΔP of 25 psi.

It is obvious that the resulting low sulfur level in the fuel gas, after conversion to sulfur dioxide in the catalytic burner, is far below the permissible emission limit.

Nitrogen Oxides

The venturi particulate scrubber will remove most of the ammonia in the fuel gas so that little fuel NO_x will be formed. The temperature in the catalytic burner is low, about 1200°F , so that

little if any thermal NO_x is formed⁸. The result is that final NO_x emissions are well in compliance.

MAGNETOHYDRODYNAMIC POWER PLANT

This power plant, shown in Figures 9 and 10 is completely different from those discussed heretofore. Coal is burned in a three stage combustor. The first stage operates with about 50% of stoichiometric oxygen and rejects molten slag. The second stage operates at about 95% of stoichiometry with additional slag rejection and is followed by a third stage where seed material (a mixture of potassium sulfate and carbonate) is added. After generating direct current electricity in a channel, the plasma is finally combusted at about 105% stoichiometry with added air with additional slag and seed rejection. Steam is raised by the hot gas to generate alternating current electricity. Particulate matter is removed for recovery of the seed material and the gas is discharged to the atmosphere.

Particulates

Despite the rejection of slag, the addition of seed material results in a very high particulate loading in the raw gas. An ESP with an SCA of 500 is used to remove the solids down to the compliance limit. An unusually large SCA is required because of the high electrical resistivity of the seed compounds.

Sulfur Oxides

The seed material serves a dual purpose. The potassium contributes conductivity to the plasma followed by the potassium from the carbonate reacting with sulfur dioxide to form additional potassium sulfate. This reaction is essentially quantitative, so that provision of sufficient potassium carbonate can result in the emission of essentially no sulfur oxides.

Nitrogen Oxides

An MHD combustor operates so much hotter than a usual furnace, 4500°F versus 2500°F, that copious amounts of NO_x are formed, up to ten times as much as from a PC furnace, despite the initial substoichiometric combustion. Controlled slow cooling of the gas and recirculation of flue gas to hold down the temperature of final combustion results in a reduced final NO_x emission, one which meets the standard.

DISCUSSION

All of the power plants considered have been designed to meet or better the emission rate performance standards for air emissions as shown in Table 2. The fossil fueled power plant will just meet the standards. The low temperature of combustion and NO_x decomposition reactions inherent in PFBC account for its low NO_x emissions. The baghouse used for final particulate cleanup accounts for the low particulate emissions. The combined cycle

power plant will satisfy SO_x regulations but should be below those for NO_x and particulate matter. The magnetohydrodynamic power plant will emit essentially no SO_x while the particulate and NO_x emissions will meet standards. The fuel cell power plant will have the lowest emissions of all due to the rigid requirements of the fuel cells and the use of a low temperature catalytic burner.

The above paragraph was based on emission rates. Considering the absolute amounts of regulated pollutants emitted, shown in Table 3, the fossil fueled plant will emit the most, followed by the combined cycle and the pressurized fluidized bed combustion power plants having similar emissions, than by the magnetohydrodynamic plant, with the fuel cell power plant having by far the smallest total amount of pollutant emissions. All these emissions should have added to them the fugitive emissions from the coal pile and coal handling and preparation steps, and the ash handling steps. Considering all the emissions in Table 3, including CO_2 , hardly alters the situations.

CONCLUSION

All the subject power plants will have atmospheric environmental intrusions that are currently tolerable. The plants can be ranked, as in Table 4. This ranking is somewhat subjective. It does not take into account any weighting by the effects of one pollutant over another, which perhaps should be done. Under any ranking system, the molten carbonate fuel cell and the magnetohydrodynamic plants can hardly be dislodged from their placings and the pulverized coal plant will probably always be lowest ranked.

TABLE 3
EMISSION AMOUNTS FROM COAL CONVERTORS
(LB/HR)

<u>PLANT</u>	<u>PARTICULATE</u>	<u>SO_x</u>	<u>NO_x</u>	<u>CO₂</u>
PC	147	2940	2940	995,000
PFBC	128	2560	850	958,000
CGCC	138	2750	920	931,000
MCFC	~0	~0	~0	640,000
MHD	123	~0	2470	880,000

TABLE 4
COAL CONVERTORS EMISSION RANKING
(BEST TO WORST)

MOLTEN CARBONATE FUEL CELL

MAGNETOHYDRODYNAMIC

PRESSURIZED FLUIDIZED BED COMBUSTOR

COAL GASIFICATION COMBINED CYCLE

PULVERIZED COAL

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FIGURE 1

[illegible]

NOTES:

DESIGN POINT 14701
ILLUMINATE CBL. R. 0.5 MINS AT 1500
500 WGS 7 AIR PHOT
TC-40 30 INCH L30 STEAM ILLUMINE
500 WGS-7 AIR PHOT
END EXCESS AIR

COMBUSTION POWER	308.037000
NET POWER	507.377000
PLANT EFFICIENCY	39.002

[illegible]

FIGURE 2

PULVERIZED COAL PLANT

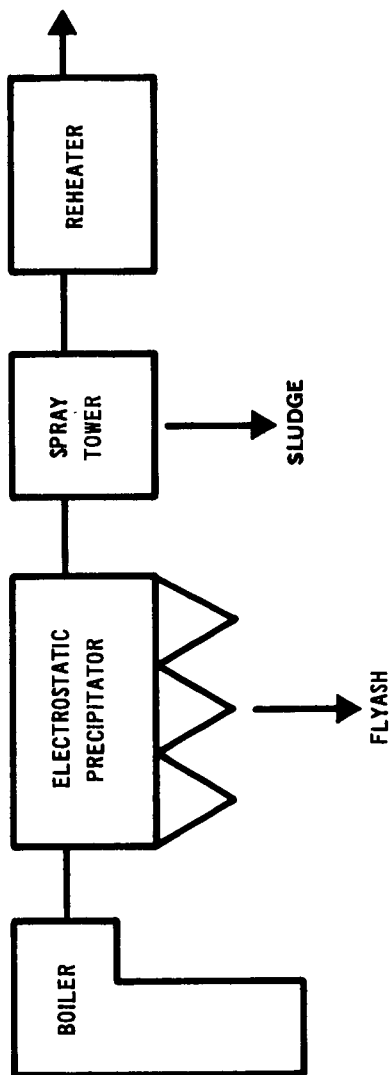


FIGURE 3
PRESSURIZED FLUIDIZED BED PLANT HEAT AND MASS BALANCE

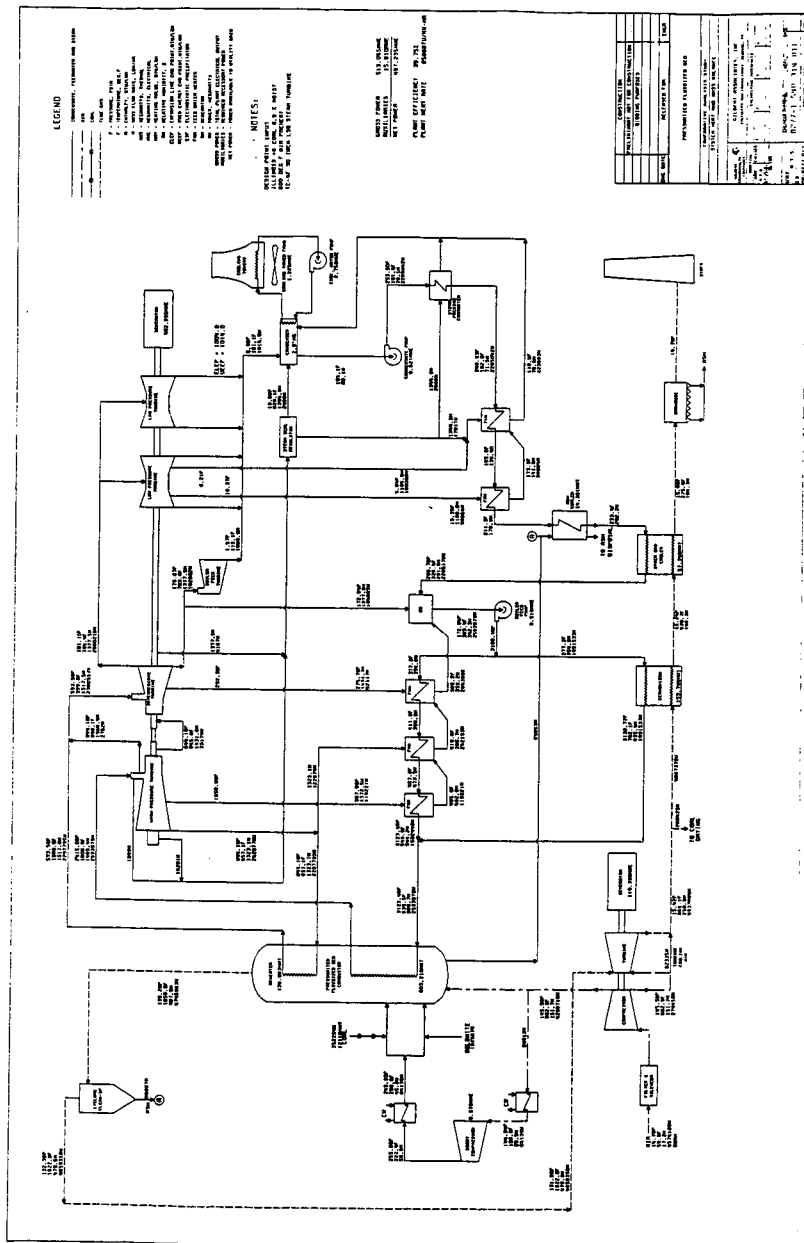


FIGURE 4

PRESSURIZED FLUIDIZED BED PLANT

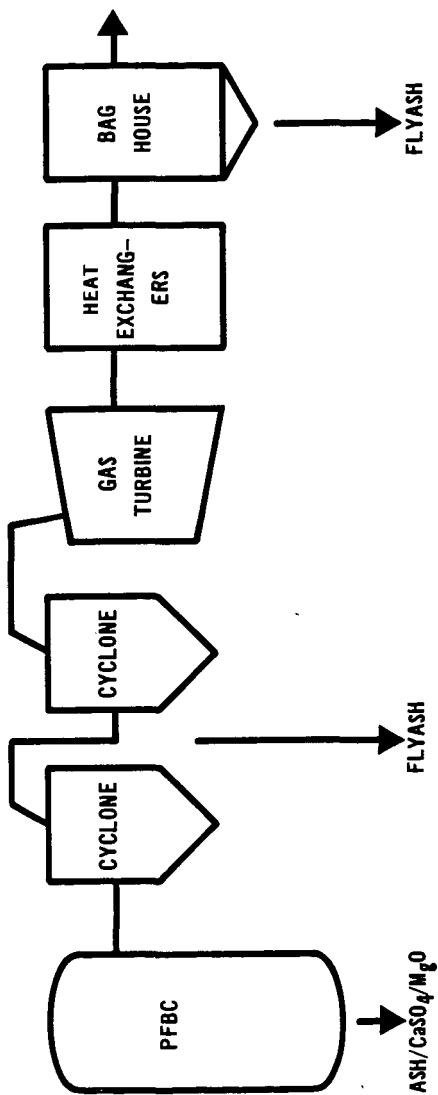


FIGURE 5
GASIFICATION COMBINED CYCLE PLANT HEAT AND MASS BALANCE

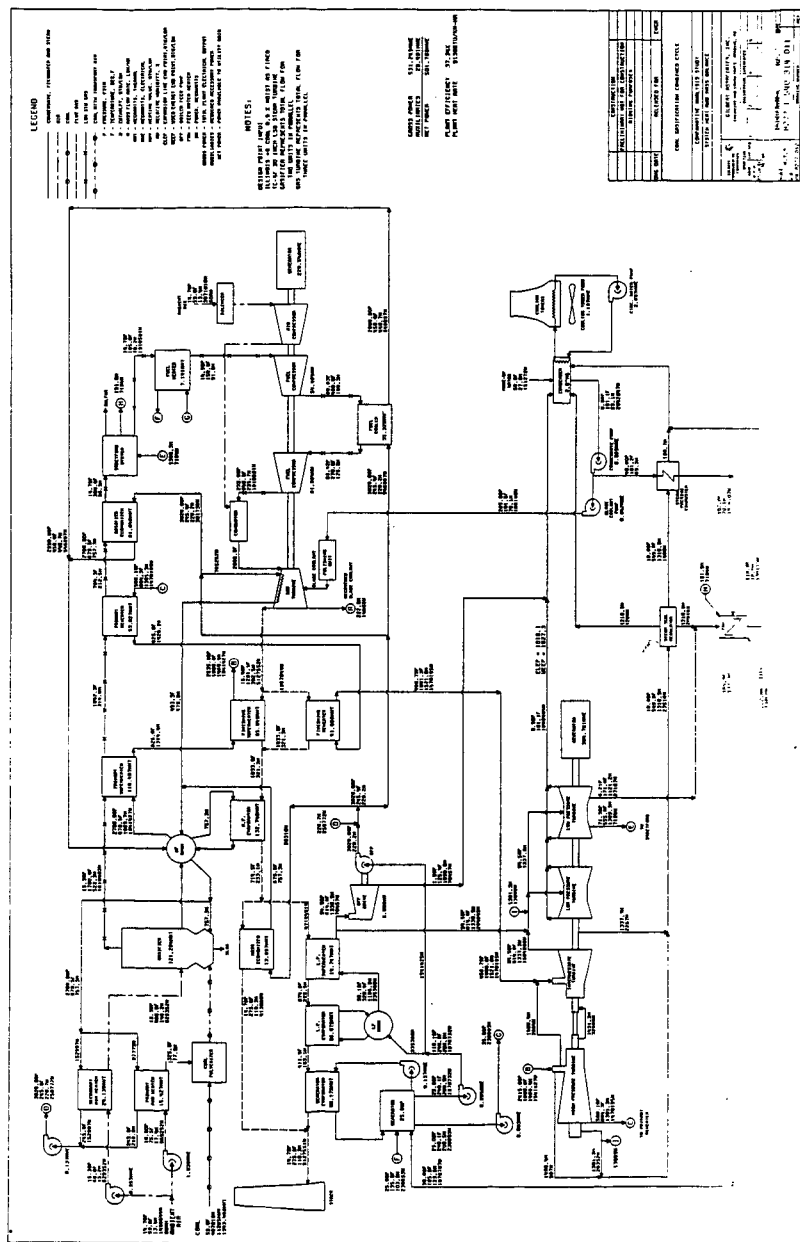


FIGURE 6

COAL GASIFICATION COMBINED CYCLE PLANT

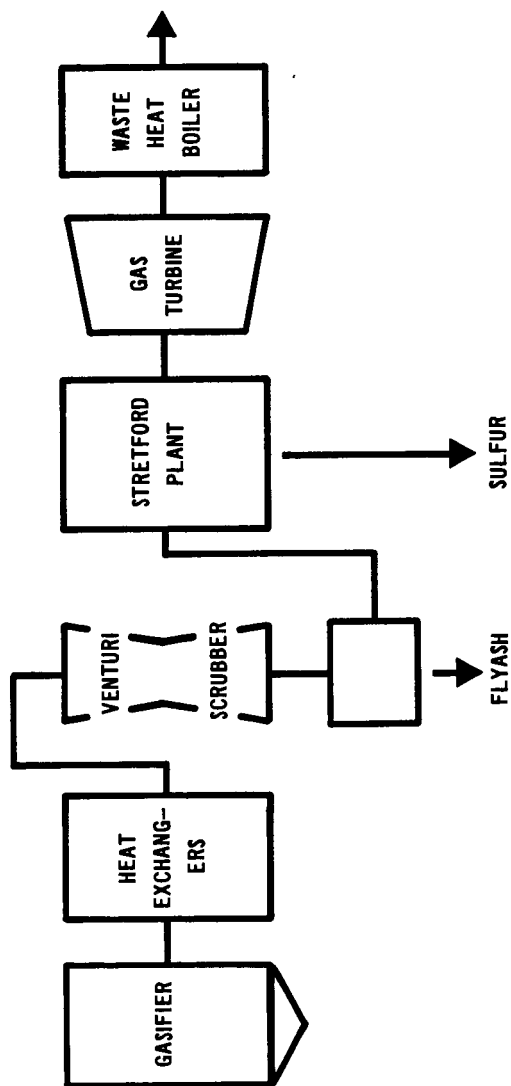


FIGURE 7
FUEL CELL PLANT HEAT AND MASS BALANCE

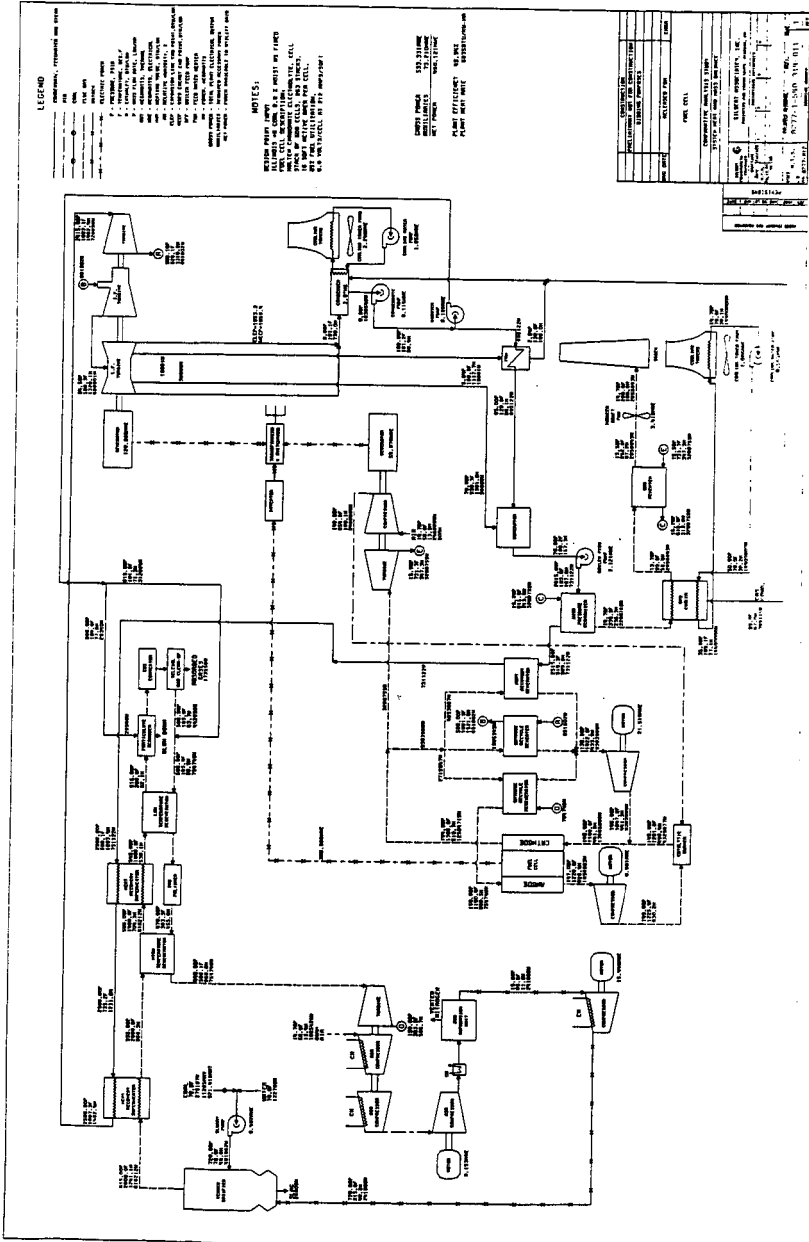


FIGURE 8

MOLTEN CARBONATE FUEL CELL PLANT

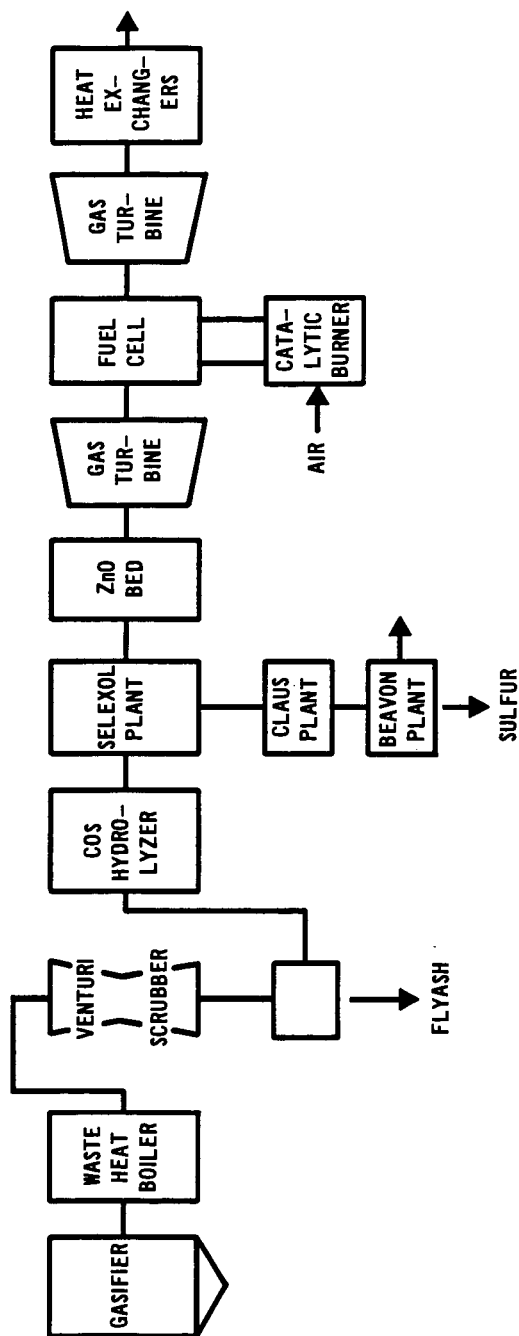


FIGURE 9
MAGNETOHYDRODYNAMIC PLANT HEAT AND MASS BALANCE

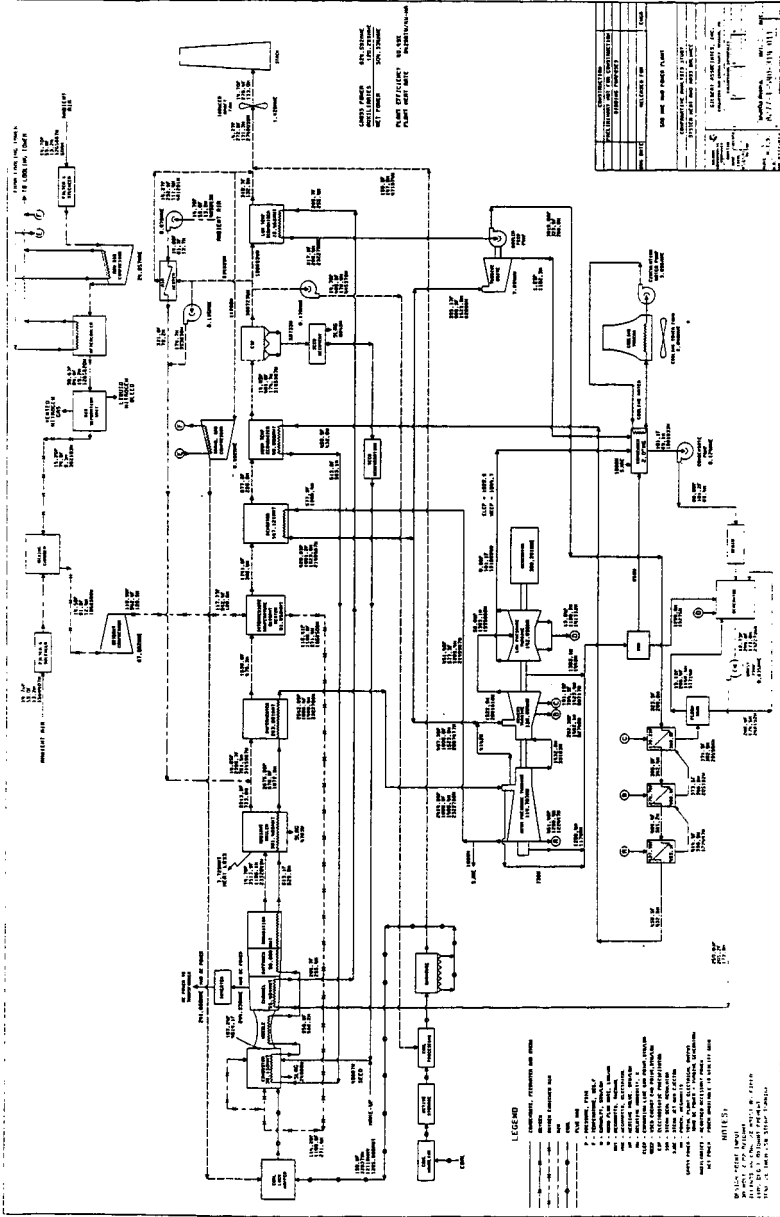
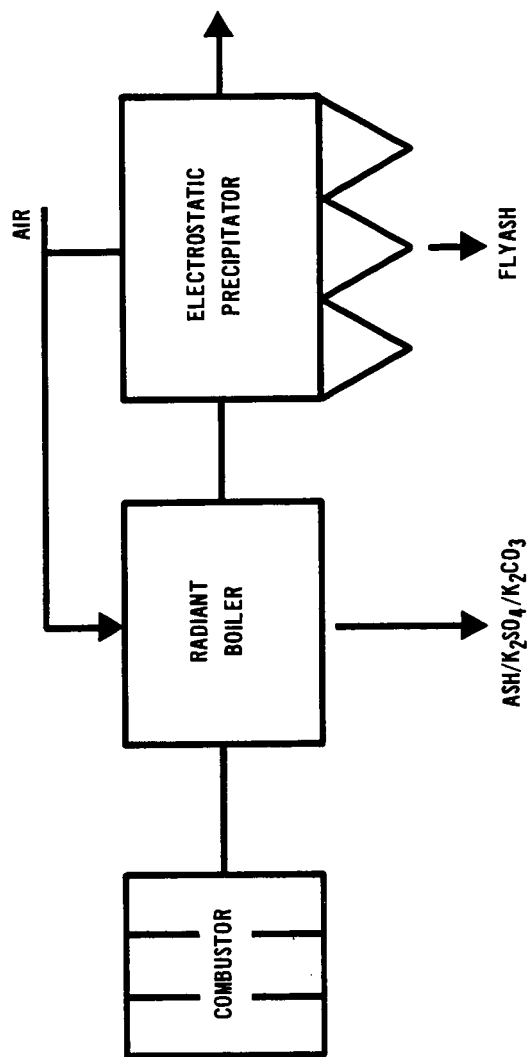


FIGURE 10

MAGNETOHYDRODYNAMIC PLANT



LARGE-SCALE PEAT FEED PREPARATION

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Introduction

In 1980 the Institute of Gas Technology (IGT) installed large-scale drying, grinding, screening and transport equipment for processing of Minnesota peat in an existing pilot plant designed to produce substitute natural gas (1). The facility, located at IGT's Energy Development Center in Chicago, is capable of drying 16 tons per hour of as-received-peat (60-75 wt % moisture content) to a controlled product-moisture-content ranging between 5 and 50 wt %. Subsequent screening and grinding operations produce a -20+80 USS mesh size product for injection into the fluidized bed gasifier. See Figure 1.

Since this was the first large-scale attempt in this country to prepare and transport peat at moisture levels as low as 5 wt %, two major questions were asked: 1) What procedures and what type of equipment would be required to process, transport and store peat, and 2) what affect would these operations have on the physical and chemical characteristics of the peat?

The successful operation of the peat feed preparation system (2000 tons of wet peat processed) provided these answers. The results of these efforts are summarized in this paper.

Design Conditions

Since the selection of appropriate equipment and the definition of handling precautions were prerequisites of the design phase, IGT's process development group concentrated its initial efforts in this area. The selection of drying equipment, capable of providing a wide range of product moisture contents, received the highest priority. One of the most important selection criteria was the ability to moderate temperatures sufficiently such that the chemical composition of the peat would not be affected even when dried to 5 wt % moisture. Both foreign and U.S. companies were contacted and all commercially available equipment evaluated. The types of dryers considered included: rotary drum dryers, flash dryers, and fluidized-bed dryers. Grinding and screening equipment was also evaluated. Design considerations included the ability to handle a range of moisture contents, ability to handle fibrous and woody material, and minimization of fines production.

In order to identify proper handling precautions, IGT commissioned the Technical Research Center of Finland to survey available data in the Scandinavian, Russian, and German literature and to provide summary reports of their findings(2,3). These reports did indicate that additional precautions must be taken as peat moisture contents are lowered. Existing data indicated that:

- o When the moisture content is 35-40%, peat dust is only slightly susceptible to explosion and when the moisture content is 40-50%, the dust is not explosible under ordinary conditions.
- o As the moisture content decreases, the minimum explosible concentration of peat dust decreases.
- o As the moisture content decreases, the maximum pressure and the maximum rate of pressure rise of the peat dust explosion increase.

- o As the moisture content decreases, the minimum ignition energy of the peat dust cloud also decreases.

Commercial experience also provided the following recommendations:

- o Operate continuous rather than batch processes.
- o Isolate high risk equipment.
- o Design mass flow systems for small quantities.
- o Locate equipment outdoors.

As a result of these investigations and recommendations, a final process configuration was selected for the peat preparation facility.

Process Description

Figure 2 presents the equipment selected for the peat feed preparation facility. Peat is received untreated from the bog and stored at the site in an outdoor storage area. In order to facilitate handling, the peat is first dried and then screened and ground to the proper size consistency. A triple-pass rotary drum dryer was chosen to provide the necessary flexibility in drying capacity. See Figure 3. Peat is, for the most part, conveyed by the hot flue gases through the multiple-pass system. Large particles, which require longer residence times to achieve the same moisture reduction, are hindered sufficiently to obtain the necessary drying time. A 50 million Btu/h natural gas burner provides a hot, co-current air stream with a maximum initial contact temperature of 1200°F. Moisture content of the peat is controlled by the exit air temperature, which typically ranged between 110° and 260°F for moisture contents between 40 and 5 wt %.

Since the dryer system presents the highest risk for dust ignition, isolation was provided by rotary valve seals. In addition, a steam quenching system and relief doors were provided as additional safeguards. Sealed screw conveyors and a bucket elevator were used to transport the dried peat to the screening and drying system. Conventional screeners and a hammer mill were chosen to size the product. An overall view of the peat preparation facility is shown in Figure 4.

Product peat was then delivered to either a high-pressure, lockhopper feed injector (4), slurry preparation or 400-ton storage silos. All storage bins were purged with nitrogen to provide an inert atmosphere and were monitored for oxygen content. These design considerations have resulted in the controlled production of peat containing moisture contents as low as 5 wt % in a reliable and safe manner.

Test Results

Once operation of the facility was begun, data were collected to determine the effects on the physical and chemical properties of the peat during the various processing steps. Minnesota peat, obtained from the Northern Peat Company, Grand Rapids, Minnesota, exhibited a remarkable uniformity in chemical composition and moisture content. Average values for size distribution and chemical composition and the standard deviation for a sample size of seven are given in Tables 1 and 2. Of greatest concern was the occasional lacing of the 'raw' peat with semi-decomposed tree roots and stumps, as well as gravel picked up during harvesting operations in the field. These materials were removed by a 2x2 stationary screen.

One of the main design considerations for the selection of the drying system was to minimize overheating and chemical degradation of the peat particle during drying. Samples of peat exiting the dryer were routinely taken and analyzed for chemical composition. Table 3 compares values at moisture levels of 5.3, 10.1, 16.0, and 22.0 wt % against those of raw peat containing 68.9 wt % moisture. It can

be seen that no significant change in chemical composition occurs during the drying operation.

Size distribution changes do occur as peat is dried. Table 4 and Figure 5 provide a comparison of sieve analyses for various moisture levels exiting the dryer. Sufficient size reduction occurs to warrant screening prior to grinding to a -20+80 USS product size.

Another issue of interest is the homogeneity of the moisture level for the peat exiting the drying system. Figure 6 indicates the variation in moisture content as a function of particle size for various peat samples exhibiting average moisture levels of 30, 36, and 42 wt %. This is particularly important in cases where downstream processing would tend to encourage segregation. For instance, screening area requirements can be affected by both the feed rate, particle shape and moisture content of the peat.

Similar concerns were raised about the chemical composition variation as a function of particle size. Data taken of the product, fines and oversize streams from the screening operation (Table 5) do not indicate any significant difference in chemical composition.

Summary

Data collected during an operating period which processed over 2000 tons of as-received Minnesota peat have shown that peat can be dried, screened and finely ground in a reliable and safe manner. Moisture reduction to as low as 5 wt % can be obtained in properly designed systems without chemical degradation of the product. Some reduction in the size distribution of the Minnesota peat did occur during the drying operation. In addition, the moisture content of the product is not completely homogeneous. Moisture content does vary with particle size, however, chemical composition does not vary significantly with particle size. These findings were subsequently used in evaluating process and equipment requirements for downstream operations in the gasification pilot plant. Segregation, for instance, of the product peat was discouraged in order to ensure uniform levels of moisture in the feed to the gasifier.

Acknowledgement

The work presented in this paper was jointly funded by the U.S. Department of Energy and the Gas Research Institute.

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Table 1. AVERAGE SIZE DISTRIBUTION FOR AS-RECEIVED MINNESOTA PEAT

<u>Screen Analysis, U.S.S., wt %</u>		<u>Standard Deviation</u>
+ 10	42.3	4.6
+ 20	25.6	2.1
+ 30	9.2	1.1
+ 60	12.9	3.9
+ 80	3.7	1.0
+100	2.1	0.8
+200	1.2	0.4
+230	2.1	0.5
PAN	<u>0.9</u>	0.6
TOTAL	100.0	

Table 2. AVERAGE CHEMICAL COMPOSITION FOR AS-RECEIVED MINNESOTA PEAT

<u>Chemical Analysis, wt %</u>		<u>Standard Deviation</u>
Proximate (Dry)		
Volatile Matter	59.4	1.1
Fixed Carbon	23.2	1.3
Ash	<u>17.4</u>	1.2
TOTAL	100.0	
Moisture	68.9	1.0
Ultimate (Dry)		
Carbon	48.3	1.3
Hydrogen	5.0	0.2
Sulfur	0.3	0.05
Nitrogen	2.1	0.1
Oxygen	26.9	0.7
Ash	<u>17.4</u>	2.2
TOTAL	100.0	

Table 3. COMPARISON OF PEAT CHEMICAL COMPOSITION AT VARIOUS MOISTURE LEVELS

Description	RAW* PEAT	SDEV**	DRIED PEAT	SDEV	DRIED PEAT	SDEV	DRIED PEAT	SDEV	DRIED PEAT	SDEV
Moisture, wt %	68.9	1.0	5.3	0.2	10.1	1.4	16.0	1.1	22.0	2.4
Proximate Analysis (Dry), wt %										
Volatile Matter	59.4	1.1	59.1	1.1	59.1	1.4	59.6	1.1	59.6	0.8
Fixed Carbon	23.2	1.3	23.6	0.7	23.5	1.2	23.5	1.1	23.6	1.0
Ash	17.4	1.2	17.3	1.1	17.4	1.8	16.9	0.7	16.8	0.6
TOTAL	100.0		100.0		100.0		100.0		100.0	
Ultimate Analysis (Dry), wt %										
Carbon	48.3	1.3	48.2	0.6	48.4	0.8	48.7	0.5	48.2	0.4
Hydrogen	5.0	0.2	5.0	0.1	5.0	0.1	5.0	0.1	5.1	0.1
Sulfur	0.3	0.05	0.3	0.08	0.3	0.07	0.3	0.08	0.2	0.05
Nitrogen	2.1	0.1	2.2	0.1	2.2	0.1	2.3	0.2	2.2	0.1
Oxygen	26.9	0.7	27.0	0.5	26.7	0.9	26.8	0.5	27.5	0.3
Ash	17.4	2.2	17.3	1.1	17.4	1.8	16.9	0.7	16.8	0.6
TOTAL	100.0		100.0		100.0		100.0		100.0	

* As-received from bog.

** SDEV = Standard Deviation

Table 4. COMPARISON OF PEAT SIZE DISTRIBUTION AT VARIOUS MOISTURE LEVELS

Description	RAW PEAT	* SDEV		DRIED ¹ PEAT		SDEV		DRIED PEAT		SDEV		DRIED PEAT		SDEV	
		Moisture, wt %		Screen Analysis, U.S.S., wt %											
	68.9	1.0	5.3	0.2	10.1	1.4	16.0	1.1	22.0	2.4					
+ 10	42.3	4.6	9.2	1.8	13.7	5.4	12.7	1.4	11.9	3.0					
+ 20	25.6	2.1	27.4	5.3	27.2	2.9	33.8	5.0	29.9	3.0					
+ 30	9.2	1.1	15.4	2.9	13.6	1.3	16.7	0.8	14.0	2.7					
+ 40	--	--	13.2	3.8	12.1	2.9	8.8	4.4	11.7	0.7					
+ 60	12.9	3.9	18.5	3.8	16.6	3.3	16.3	3.8	16.0	3.1					
+ 80	3.7	1.0	4.7	1.3	5.4	1.9	3.9	1.1	5.7	0.3					
+100	2.1	0.8	3.1	0.7	3.8	1.9	2.6	1.0	2.8	0.2					
+200	1.2	0.4	4.6	1.7	4.0	0.9	1.9	1.2	3.7	1.6					
+230	2.1	0.5	1.3	0.9	1.3	1.7	1.5	0.9	1.5	0.9					
PAN	0.9	0.6	2.6	0.6	2.3	0.3	1.8	0.5	2.8	0.9					
TOTAL	100.0		100.0		100.0		100.0		100.0						

* SDEV = Standard Deviation

Table 5. COMPARISON OF CHEMICAL COMPOSITION FOR PEAT OF DIFFERENT SIZE FRACTIONS

Description	<u>DRYER DISCH.</u>	<u>FINES</u>	<u>OVER SIZE</u>	<u>SIZED PRODUCT</u>
Mass Fraction, wt % (U.S. Sieve)				
+20	30.1	0.1	93.5	3.5
-20 to +80	53.0	7.6	6.1	94.0
-80	16.9	92.3	0.4	2.5
Proximate Analysis, wt %				
Volatile Matter	59.4	57.0	60.2	58.7
Fixed Carbon	25.0	23.0	24.3	24.6
Ash	<u>15.6</u>	<u>20.0</u>	<u>15.5</u>	<u>15.7</u>
TOTAL	100.0	100.0	100.0	100.0
Ultimate Analysis, wt %				
Carbon	49.3	46.7	49.3	49.2
Hydrogen	5.1	4.9	5.1	5.2
Sulfur	0.4	0.3	0.3	0.3
Nitrogen	2.2	2.2	2.1	2.2
Oxygen	27.4	25.9	27.7	27.4
Ash	<u>15.6</u>	<u>20.0</u>	<u>15.5</u>	<u>15.7</u>
TOTAL	100.0	100.0	100.0	100.0
Moisture, wt %	7.1	7.9	11.4	7.7
Bulk Density, lb/ft ³	27.8	30.1	26.6	26.8

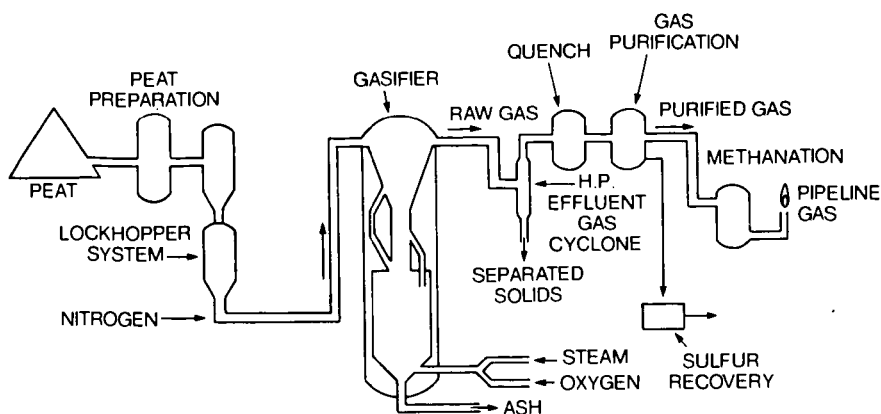


Figure 1. PEATGAS PILOT PLANT FACILITY

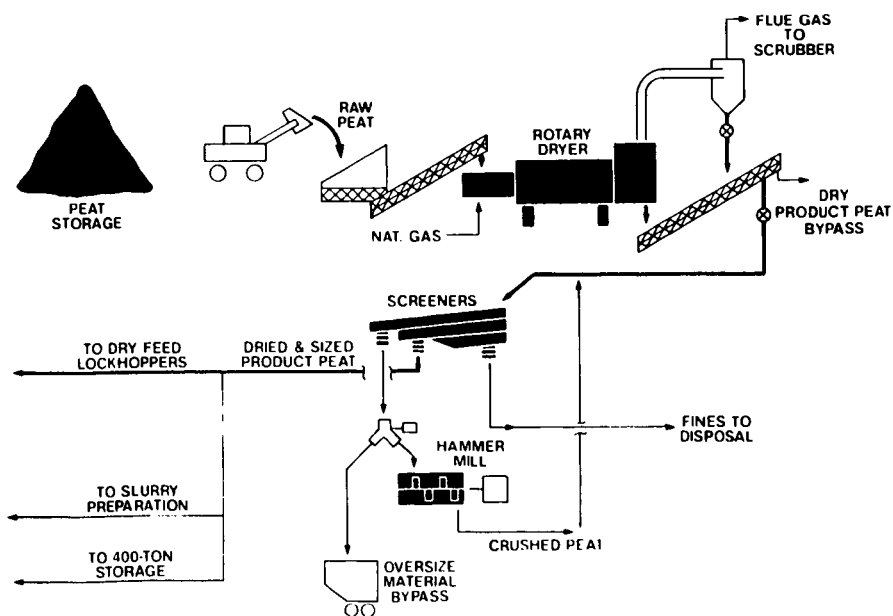


Figure 2. PEAT PREPARATION

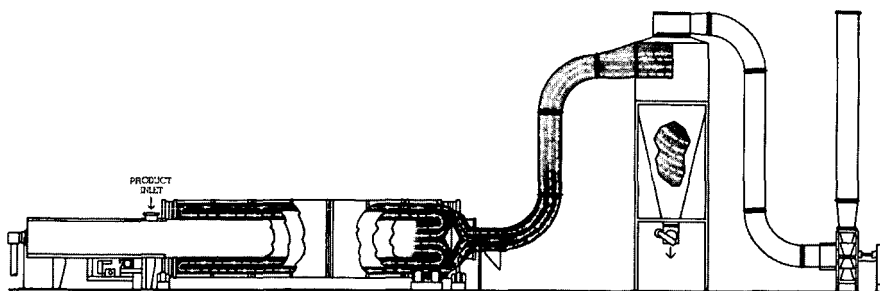


Figure 3. TRIPLE-PASS DRYER SELECTED FOR THE PEAT DRYING SYSTEM

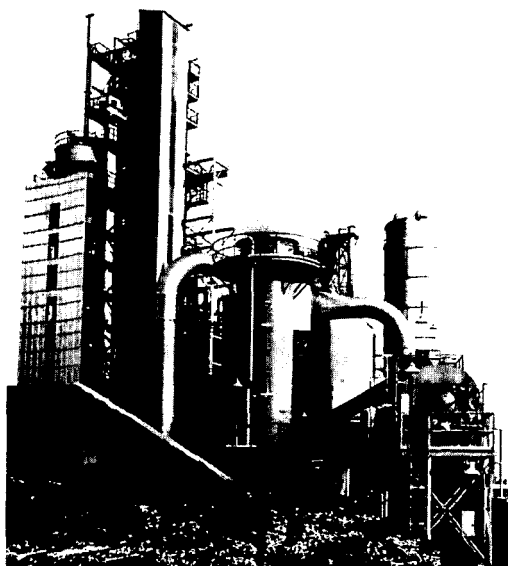


Figure 4. DRYING SYSTEM IN OPERATION

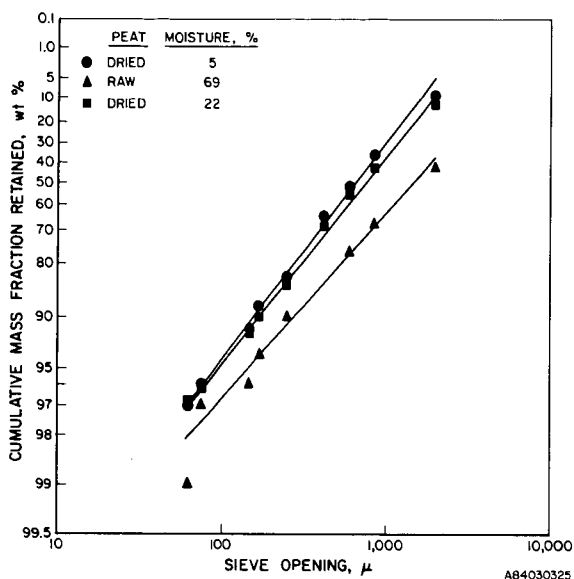


Figure 5. GRAPHICAL REPRESENTATION OF THE SHIFT IN SIZE DISTRIBUTION OF DRIED PEAT

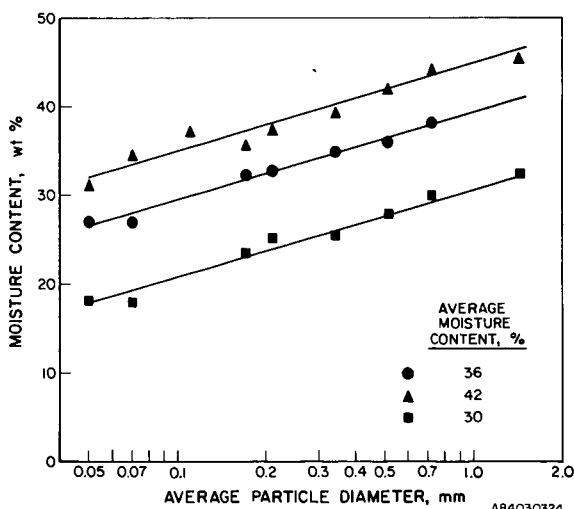


Figure 6. PEAT MOISTURE CONTENT AS A FUNCTION OF PARTICLE SIZE FOR SAMPLES EXHIBITING AN AVERAGE MOISTURE CONTENT OF 42, 36 AND 30 wt %

MULTIPLE MECHANISMS FOR LOSS OF COAL COKING
PROPERTIES CAUSED BY MILD AIR OXIDATION

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There are at least three different mechanisms responsible for the loss of coal coking properties caused by mild air oxidation, weathering. We present here data demonstrating their existence. The chemical changes responsible for the coking loss are only partly characterized. In no case is it understood how they destroy or diminish a coals ability to coke.

We worked with Bruceton coal, a high quality, unoxidized sample provided by the kind folks at PETC. Weathering for more than 250 days at 25 °C and 50% relative humidity produced no change in the free swelling index, and only small changes in the coal. When weathered at 80 °C and a water pressure of 12 mm, the FSI declined as shown in Fig. 1. The swelling of the weathered coal in pyridine is also shown in Fig. 1, and remains constant while the FSI is decreasing. The subsequent decrease in swelling is interesting, but not relevant to the issue under consideration here, that of the causes of the observed decrease in FSI.

A sample of coal weathered for 28 days was treated with lithium aluminum hydride (LAH) following the lead of Orchin et. al.(1). As reported(1), the original FSI of the coal was restored. In this case the FSI went from 3 to 8. There exists a weathering pathway which is rapid and readily reversible by LAH reduction. As we will show in subsequent papers, it involves formation of carbonyl and carboxyl groups. This is the first mechanism.

A sample of the same coal weathered for 220 days was subjected to the same procedure. The FSI before reduction was 0.5 and after reduction was 2. Clearly a second mechanism is operative, one which cannot be reversed by LAH reduction.

These mechanisms do not involve any changes in the coal's cross-link density, as shown by the constant swelling in pyridine during the changes in FSI. The third mechanism does involve changes in the cross-link density. It was reported first by Liotta who worked with Ill. No. 6 coal(2). As the coal weathered, the cross link-density increased. Liotta ascribed this to ether linkages, but this has been questioned(3). Unfortunately, a detailed description of the weathering conditions was not provided. At 25 °C, we see no

change in the cross-link density of Ill. No. 6 coal due to weathering, but do see an increase in cross-link density as reported by Liotta when the coal is weathered at 150 °C. Thus there exists a third weathering mechanism, the one originally reported by Liotta and one which involves changes in the macromolecular structure of the coal.

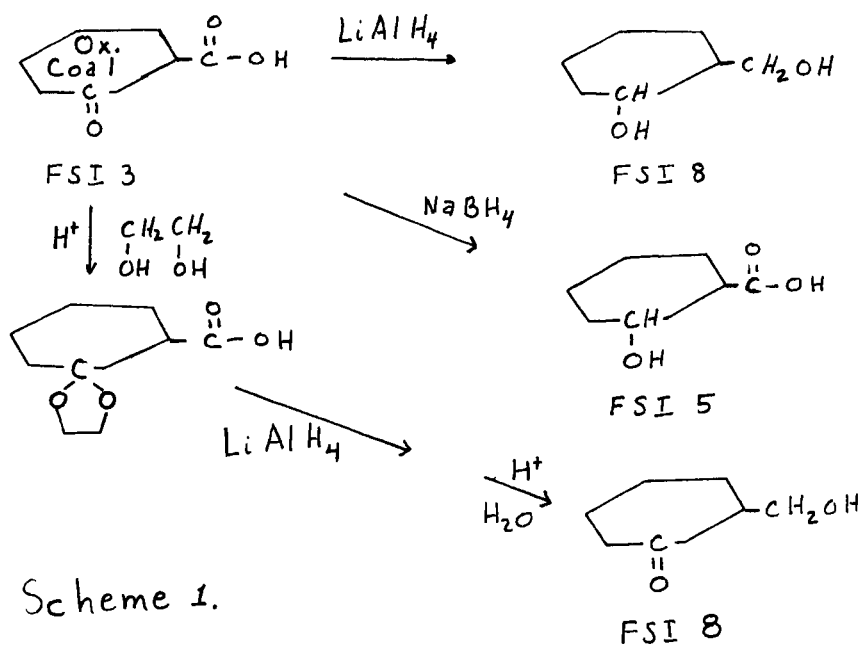
The first two mechanisms have been partly characterized. Using the chemistry shown in Scheme 1, 28 day oxidized Bruceton coal was prepared and the carbonyl groups and the carboxyl groups independently and selectively were reduced. It is clear from the data shown in the scheme that carboxyl groups are more important than carbonyls in the destruction of coking properties.

We thought that changes in the coal's bitumen might be contributing to mechanism two, since the pyridine extractables decreased, roughly paralleling the slow loss of coking ability. Accordingly, the pyridine extract from unoxidized Bruceton coal was added to the 220 day oxidized coal. Adding the extract by soaking the coal in a pyridine solution of the extract and then evaporating the pyridine had a smaller effect on the FSI than grinding the solid coal and extract together. This is consistent with the large amount of surface chemistry involved in these oxidations, a point we will take up in later papers. After grinding with 22% (wt) of extract, the FSI of 220 day oxidized coal was 4. It was 2 before grinding and the increase is due to the addition of a good swelling component, the extract which has an FSI of 5. Removal of the pyridine extractables from the unoxidized coal causes a sharp decline in the FSI, but grinding with the extract causes the FSI to return to its initial value. Clearly changes in the bitumen are not responsible for the loss of coking ability. We hope to know more about this pathway when we present our paper, but are not optimistic.

Acknowledgement. We thank the Gas Research Institute for support and its employees for encouragement, good advice, and cooperation.

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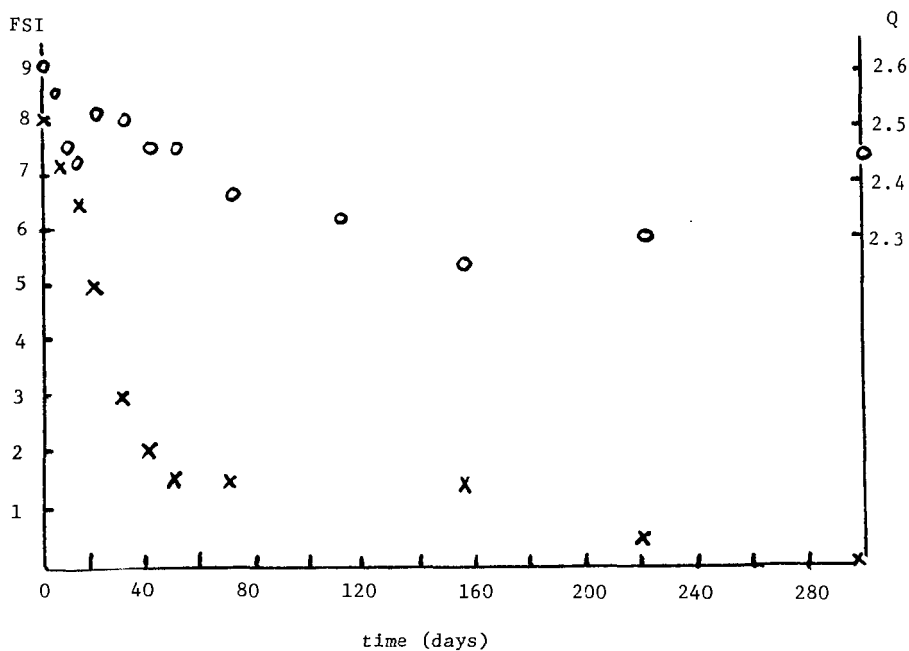


Fig. 1. Change in Free Swelling Index (x) and Volumetric Swelling in Pyridine (o) During Air Oxidation of Bruceton Coal at 80°C.

CHEMICAL COMMINUTION OF COAL

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ABSTRACT

Chemical comminution is an effective means for size reduction and beneficiation of coal. Sodium hydroxide and i-propanol show synergism in chemical comminution of Illinois No. 6 bituminous coal.

The system was effective at low alkali concentrations with low consumption of NaOH. Much of the NaOH consumed was for neutralization of acidity of the coal. Isopropanol serves only as a reaction medium and could be recovered nearly quantitatively for recycle. The system lends itself to application in preparation of coal-water mixture and coal-alcohol slurry fuels.

* * *

INTRODUCTION

The use of coal as a source of energy and hydrocarbons will become more important in the future. In the upgrading and utilization of coal, size reduction is an important preparative step. The beneficiation of coal needs extensive crushing and the preparation of coal-water fuel mixtures, requires even finer particle size. Size reduction by mechanical means is not only energy intensive but also causes heavy wear on the processing equipment.

An alternative method of coal comminution is to weaken the coal structure by chemical action. This concept has been applied to remove mineral matter from coal (1), to desulfurize coal (2,4,5) and to facilitate in-situ coal extraction from underground deposits (6).

Various reagents which have been studied for chemical comminution include pure and aqueous ammonia, alkals such as NaOH, KOH, Na_2CO_3 , $\text{Ca}(\text{OH})_2$, etc. and organic solvents (3,7). The common limitations of the above-mentioned approaches are high reagent consumption and a low degree of effectiveness.

Among the systems studied, NaOH in high concentration (>0.1 N) is one of the most promising. However, the NaOH consumption is >5 wt% of treated coal and this makes it unattractive for practical applications.

We discovered that NaOH and i-propanol show synergism in coal comminution and that coal can be effectively comminuted by NaOH at concentrations less than 0.1 N in 90% i-propanol/water, with a low alkali consumption. The alcohol is not consumed chemically in the process and can be recovered quantitatively for reuse. The mechanism and kinetics of coal-alkali reactions were also investigated.

EXPERIMENTAL

Coal Sample: Illinois No. 6 Bituminous Coal, with the size in the range of 1-1.2 cm³ were hand-picked for the experiments.

Comminution Solution: Reagent grade NaOH and i-propanol were used as received. The comminution solution was prepared as a 9 to 1 volume ratio of i-propanol to aqueous NaOH stock solution. The different NaOH concentrations of the comminution solution were obtained by varying the concentration of NaOH stock solutions. The normality of the NaOH solution is calculated based on the total volume of the caustic and iso-PROH.

Coal Comminution Procedure: Seventy-five ml of comminution solution and 10 g of coal were reacted in a sealed stainless steel vessel at 100°C for 48-86 hours. The treated coal was recovered by filtration and dried in a 100°C oven overnight.

The effect of chemical comminution was judged by the following standards:

- o Very extensive: Coal sample is disintegrated into 10 or more smaller pieces.
- o Extensive: Coal sample is disintegrated into less than 10 pieces of smaller coal.
- o Good: Little coal is degraded. Coal has well developed cracks all over the surface and samples can be crumbled with hand pressure.
- o Fair: Little or no smaller coal pieces are found. Cracks on coal surface are formed mainly along the seam.

The pH values of the initial and spent solution were analyzed with a pH meter. The NaOH concentration of the corresponding solutions were determined by titration.

Determination of i-propanol Consumption: A thick-walled Pyrex tube divided into two compartments with a medium porous glass frit in the middle was employed. Comminution solution (50 ml) was first introduced into the tube and allowed to drain through the frit and fill the lower compartment. Coal (60-100 mesh, 10 g) was then charged into the upper compartment. After the tube was sealed, the tube was inverted to allow the comminution solution to contact the coal. The sealed tube was heated at 100°C at this position for 48 hrs.

After the heating period, the sealed tube was inverted back to its original position to disengage liquid and solid. The coal was dried by freezing the liquid compartment in liquid N_2 and heating the coal compartment with wrapped heating tape. The coal and the solution were recovered by opening the sealed tube and their weights were determined. The i-propanol content in the solution was determined by gas chromatography. A series of experiments consisting of three repeats averaged 99% material balance and i-propanol consumption was 0.1-0.7%.

Determination of NaOH Consumption Rate: A Brinkmann autotitrator E526 was used. Coal (0.5 g, 200+ mesh) was suspended in 50 ml of 90% i-propanol aqueous solution under an argon atmosphere and titrated against 0.01 N NaOH at a pH of 7.

Determination of the Neutralization Equivalent of Coal: Aliquots of 1 ml, 0.5 N NaOH were added to 5 g of coal (200 mesh) suspended in 50 ml of 90% i-PROH. The pH change was followed by a pH meter. Additional NaOH was added when the pH dropped below 7. This procedure was repeated until a steady pH of 7 was reached.

RESULTS AND DISCUSSION

Synergism of NaOH and Alcohols: Alcohol by itself is a very weak comminution agent. Storing coal under alcohols such as methanol, ethanol and i-PrOH for an extended period of time does not weaken the coal structure. Similarly, sodium hydroxide at concentrations lower than 0.1 N is not an effective comminution agent.

It is found in this study that by combining those two ineffective agents, an efficient comminution solution was obtained. Thus, dilute NaOH at levels of 0.025-0.1 N in 90% i-propanol is very effective for comminuting coal with low alkali consumption. Without i-propanol, the concentration of NaOH at these levels is too low to comminute the coal. In the presence of i-propanol, extensive comminution is achieved with low alkali consumption. To achieve these levels of comminution without i-propanol, the NaOH consumption would have been 6.2 wt% of treated coal for 0.1 N NaOH solution. In the presence of isopropanol the typical levels of alkali consumption are in the range of 0.7-2.0 wt% of treated coal (Table 1). For example, the NaOH consumption for an extensive comminution is 2.6% for 0.1 N NaOH in 90% i-PrOH.

The much enhanced comminution effect of NaOH-i-PrOH relative to aqueous NaOH is due to several possible causes:

1. As polar organic compounds, alcohols wet coal better than water and facilitate the contact between alkali and coal. The observed trend in terms of effective comminution medium is:



Apparently higher alcohols are better comminution solvents due to their higher affinity to and more effective wetting of the coal surfaces.

2. The reactivity of the OH^- anion may be enhanced by the solvation of Na^+ cations by alcohol molecules relative to aqueous solution so that the OH^- becomes more exposed and free to attack acidic substrates. It is well known that crown ethers, THF, polyalkylene polyamines are capable of "trapping" alkali and alkali earth cations (13). Therefore n-butyl lithium is a much stronger nucleophile in THF, crown ethers and tetramethylenediamine than in hexane.

Effect of Alkali Concentration: The initial alkali concentration was varied between 0.01 and 0.1 N. Notwithstanding the 10-fold increase in NaOH concentration, the initial pH of the comminution solution remained constant at about 12.5 (Table 1). It is suspected that the 90% i-propanol solution is saturated with NaOH at a concentration greater than 0.01 N. At NaOH concentrations greater than 0.01 N, the solutions appeared turbid.

A linear relationship exists between the initial NaOH concentration and consumption of alkali (Figure 1). The alkali consumption can be lowered by using a more dilute alkali solution but its effectiveness for comminution is reduced. The lowest NaOH concentration in 90% i-PrOH sufficient to comminute coal is about 0.028 N. The NaOH consumption in this case is 0.7 wt% of the coal. This alkali concentration probably is the most cost effective for coal comminution.

At higher NaOH concentrations, the consumption of NaOH increases as the comminution becomes more extensive. At 0.1 N NaOH concentration the degradation of coal structure was extensive and the alkali consumption reached 2.6%. This condition probably is the upper limit for economical coal comminution. (The criteria of comminution effect are defined in the experimental section.)

To obtain effective coal comminution, a minimum pH of 10 should be maintained. It is clear that run A4 and B4 (Table 1) had inadequate alkali strength to result in poor comminution. The alkali concentrations used in A3 and B3 are optimum for good comminution effects.

Alkali Consumption: The alkali consumed in the chemical comminution in the presence of i-PrOH is mainly for neutralization of acidity (8) in the coal. Phenols (9) and carboxylic acids constitute the bulk of the acids in coal. Other materials which consume alkali are metal oxides and minerals. A pH value of 3.4 was detected for a coal/water suspension (0.5 g

of 200 mesh + coal in 50 ml H_2O) indicating the acidic nature of coal.

Alkali consumption due to the acidity in the coal was obtained by neutralizing it exhaustively using dilute NaOH at pH 7. It took 1.4 wt% of NaOH based on coal to neutralize the coal. Since this value is very close to those runs in which extensive comminution was obtained (A2 and B2), we are tempted to conclude that much of the NaOH consumption is for neutralization of acidity in the coal.

Iso-propanol Consumption: The role of alcohol in the comminution of coal using a NaOH - i-PrOH - H_2O system is probably as a solvent which enhances NaOH reactivity rather than as a chemical reagent. By employing a sealed tube technique described in the experimental section, 99.2-99.9% of i-PrOH was recovered from the spent solution. This extremely high i-PrOH recovery rate supports that it does not react with coal functionalities. The very high recovery of alcohol could make the comminution method described in this paper viable for industrial applications.

Kinetics of NaOH Uptake: As mentioned above, much of the alkali taken up by coal is for neutralization of the acid sites of the coal. Therefore, a fast reaction between alkali and coal is expected. The uptake of alkali by coal in an iso-propanol - H_2O system at a constant pH of 7 and 25°C was studied using an automatic titrator. To simplify the analysis of kinetic data the OH^- concentration was kept constant.

Plotting the log of NaOH uptake rate against the log of the reaction time, a straight line with a slope of -0.5 was obtained (Figure 3). Thus, the rate of caustic uptake can be represented with the following equation.

$$r = 2.33 \times 10^7 t_{-0.5}$$

where r is the rate of caustic uptake, mole/sec. Kg of coal,
 t is time, sec.

The form of this equation suggests that the reaction is rapid and the reaction rate is mass transfer limited. The initial rate at reaction time of 0.01 sec is in the range of 10^8 mole/sec. Kg which is too fast for organic reactions likely to occur in this system at room temperature. A rate of 10^{-4} to 10^{-6} mole/sec. Kg is expected for typical organic reactions. On the other hand, the reaction rate of H^+ and OH^- is mass transfer limited at a rate of 10^{10} mole/sec. Kg (11). For the neutralization of weak acids in coal it is expected to be somewhat slower than that for the strong acids. A rate of 10^8 mole/sec. Kg is reasonable. This supports the assumption that neutralization of acids in coal is the major reaction in the comminution of coal.

The mechanism of the above reaction can be modeled with the reaction controlled by diffusion through the "ash" layer of a shrinking core. According to this model, and following the notation used by Levenspiel (10),
the rate of reaction $-\frac{dN}{dt}$

at any time can be expressed by

$$\frac{-dN}{dt} \left(\frac{1}{r_c} - \frac{1}{R} \right) = 4 \pi D_e C \quad (1)$$

$$t = \frac{\rho R^2}{6 D_e C} \left[1 - 3 \left(\frac{r_c}{R} \right)^2 + 2 \left(\frac{r_c}{R} \right)^3 \right] \quad (2)$$

where N is conc. of reacting OH^- ion, mole

r_c , R are the radii of the reacting core at t and the original particle, respectively, cm

D_e is the effective diffusivity, cm^2/sec

C is the concentration of OH^- ions in the bulk phase mole/cc

ρ is density of coal, g/cc

For complete conversion of a particle, the time required is

$$T = \frac{\rho R^2}{6 D_e C} \quad (3)$$

The dimensionless time $\left(\frac{t}{T} \right)$ is

$$\frac{t}{T} = 1 - \left(\frac{r_c}{R} \right)^2 + 2 \left(\frac{r_c}{R} \right)^3 \quad (4)$$

$$\frac{t}{T} = 1 - 3(1-X)^{2/3} + 2(1-X) \quad (5)$$

where X is conversion, fraction.

According to Equation 5, conversion, and in turn NaOH consumption rate was calculated as a function of time using a computer. By plotting the log of NaOH consumption rate, $\log dN/dt$ against $\log t$, a straight line with a slope of -0.53 was obtained (Figure 2). A similar plot using experimental data also yielded a straight line with a slope of -0.5 (Figure 3). The excellent agreement between the experimental and calculated values demonstrate the validity of this model. Examination of the model indicates that this linear relationship is valid up to a conversion level of about 80%.

The D_e can be estimated from the experimental data. Since the real time for $x = 0.5$ and $t/T = 0.11$ was 5400 sec., the time for complete conversion T was calculated to be 49,090 sec. according to Equation (5). The effective diffusivity D_e calculated from Equation (3) is 1×10^{-6} cm²/sec. This magnitude of diffusivity compares reasonably with literature values, e.g., the self-diffusion rates of Br⁻ in 1 and 6% cross-linked divinyl benzene (Dowex 2 anion resin) at 25°C are 9 and 4×10^{-7} cm²/sec, respectively (12). The consistent value of D_e obtained further substantiates the validity of the model.

SUMMARY

Chemical comminution is an effective method for size reduction and beneficiation of coal. Although NaOH is effective at a concentration >0.1 N, the alkali consumption can be as high as 5-10 wt % of coal treated which makes it unattractive for practical applications.

We find that there is a synergistic comminution effect when NaOH is used in combination with alcohols. Such a system is more effective than NaOH or alcohols when used separately.

This synergistic effect of NaOH/alcohol may be due to its higher affinity for coal and better penetrating ability than that of NaOH/H₂O. A higher alcohol (i-propanol) was found to be more effective than methanol probably due to its larger organic groups. Another contributing factor to the synergism might be the solvation of Na⁺ by alcohol which renders the OH⁻ more

exposed and therefore, a more reactive species. Alcohol appears not to be involved in coal-NaOH reactions, since it can be recovered almost quantitatively. Its role in comminution is a reaction medium to facilitate the OH^- /coal contact.

There is a linear relationship between initial NaOH concentration and its consumption. A higher degree of comminution was affected at higher NaOH consumption. A 0.028 N of NaOH in 90% i-PrOH was effective in coal comminution with an NaOH consumption of only 0.73% of coal. The NaOH consumption is mainly for neutralizing the acidity of the coal. The NaOH consumption for neutralization and exhaustive coal comminution were essentially the same. Studies of NaOH uptake by coal at a fixed pH of 7 using an autotitrator showed that the diffusion of alkali into coal is the rate controlling step in NaOH-coal reaction.

Coal comminution with NaOH-alcohols is effective and could find applications in coal-water slurry and coal-alcohol slurry preparations.

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Figure 1. NaOH Consumption - Initial NaOH Concentration

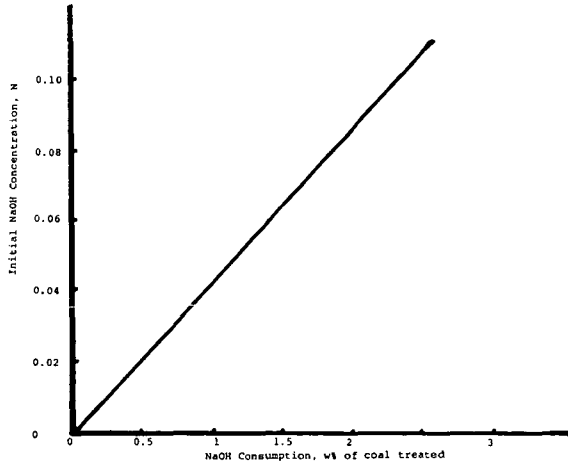
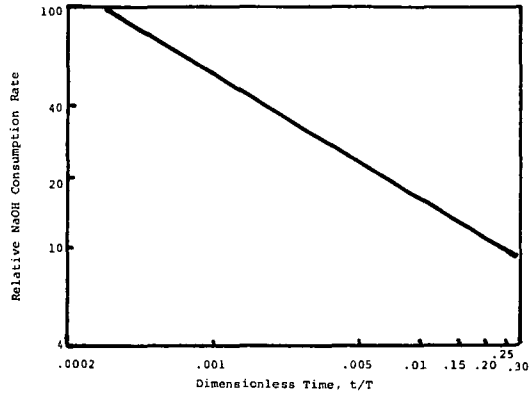


Figure 2. Predicted NaOH Consumption Rate



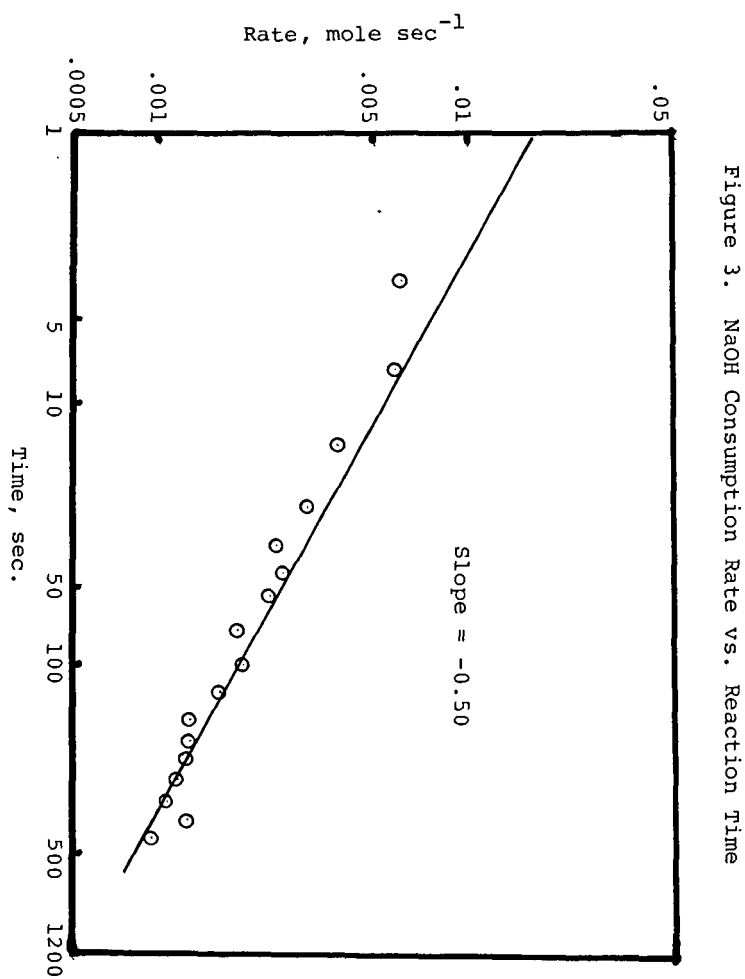


Table 1

Comminution of Illinois No. 6 Bituminous Coal
with NaOH in 90% i-Propanol

Experiment	NaOH Conc. N	Solution pH		NaOH Consumption wt% of coal	Results**	
		Initial	Final			
A*	1	0.111	12.49	11.94	2.59	Very extensive
	2	0.0456	12.49	11.94	1.2	Extensive
	3	0.028	12.48	10.62	0.73	Good
	4	0.011	12.50	8.85	0.28	Fair
B**	1	0.099	12.58	11.93	2.62	Very extensive
	2	0.0452	12.49	11.09	1.20	Extensive
	3	0.0282	12.47	10.72	0.75	Good
	4	0.0104	12.52	8.8	0.25	Fair

* 48 hr @ 100°C, 1/4-1/2 in³ coal used

** 96 hr @ 100°C, 1 in³ coal used.

Technique For Measuring Swelling Tendency and Coke Density
For Catalytic Coal Gasification

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Introduction

Since 1979, Exxon Research and Engineering Company has operated a one ton-per-day Process Development Unit (PDU) at Baytown, Texas in support of the development of the Catalytic Coal Gasification Process (CCG). Details of this process development effort are available elsewhere^{1a-c}. This paper summarizes responses of coal, particularly swelling and coke density, to gasification conditions; some characteristics of the five coals which have been processed in the PDU are given in Table 1. The PDU utilizes a high pressure fluidized bed gasifier that operates at 3.4 MPa (500 psia) and 978°K (1300°F). Coal is typically catalyzed by wet mixing with potassium salts (KOH, K₂CO₃) prior to introduction into the gasifier. The alkali catalyst promotes gasification, shift, and methanation in a single thermo-neutral reactor. Another important catalyst benefit is that it reduces the thermoplasticity of bituminous coals at the same time; however, enough thermoplasticity persists that its impact must be considered when operating a fluid bed gasifier (Figure 1). The thermoplasticity manifests itself as agglomeration which occurs during the transient plastic state and as swollen, structurally weak particles.

Because CCG conditions, viz., high heat-up rate and high pressure, are quite different from the conditions at which conventional tests for thermoplasticity are carried out, it seemed important to develop a technique which best reproduced the CCG conditions. This view is well supported in the literature. In the pyrolysis of coal, both an increase of heating rate^{2a-d} and pressure^{2b,c,e,f} have been associated with decreased viscosity or increased fluidity during the plastic transition of coal. The reduced viscosity associated with increased heating rate is normally attributed to the rapidly increasing temperature which occurs during pyrolysis. This rapid temperature increase results in an enrichment of the liquid products in the plastic mass at a higher temperature. The effect of increased pressure is to repress evolution of the low viscosity, volatile components from the plastic coal.

Typically, swelling is increased by factors that decrease viscosity during the plastic transition. There is general agreement in the literature that an increased heating rate increases the potential for greater swelling^{2a,b}. However, the influence of pressure on swelling is not as clear. Increased pressure reduces viscosity but also, because of compression, reduces the total volume of gases that are released and available to swell the plastic coal. Increasing the pressure has been reported to increase^{2b,f}, decrease^{2g}, or have little effect^{2c,h} on swelling. The differences are likely due to the different procedures and physical arrangement of the techniques used to measure swelling. Therefore, it was important for

us to choose a technique for measuring swelling that was applicable to our high pressure fluid bed in that it would be capable of differentiating good performance potential in a feed coal from marginal or unacceptable potential. In addition, the technique had to be simple and relatively fast for use as a quality control test.

This paper outlines the technique developed and illustrates the use of the test in the study of the impact of process variables of interest (catalyst, catalyst distribution, coal pretreatment, pressure, gas atmosphere) on coal thermoplasticity.

Free Fall Swelling Test

A simple, easy to use laboratory test unit was devised to study coal thermoplasticity within the context of CCG conditions. The test, known as the Free Fall Swelling Test, simulates major CCG process variables such as high pressure and high heat-up rate. A schematic of the Free Fall Unit is shown in Figure 2.

Pressure is controlled by a back pressure regulator 8 (typically between 0.1 and 3.5 MPa). Coal aliquots (150 μ m x 600 μ m, 0.25 g \pm 0.01g) are fed through a set of two valves to the hot drop tube via the feedline 3. The coal particles fall freely through the heated zone (typically operated in the temperature range of 978-1033°K) where they are rapidly heated, pyrolyzed, and form coke or char. A particle heat-up model was applied to estimate heat-up rates and free fall residence times. Time average heat-up rates range from 2,800 to 11,000°K/sec for the range of particle sizes used. The solid residue is removed from the drop tube by withdrawing the quartz liner. The use of a quartz liner allows easy and complete removal of the residue and gives visible evidence that tar evolution has ceased before the residue reaches the bottom of the liner.

On cooling, a measure is made of residue loose bulk density (equation 1) and swelling (equation 2). Generally speaking, residue densities are less than coal densities because of the combined effect of mass loss and swelling due to the transient thermoplastic state, and the densities usually vary between 0.05 and 0.55 g/cc. The Free Fall Swelling Index (FFSI, equation 2) is a measure of swelling, and it usually varies between 1.0 (no swelling) and 12.0 (a twelve-fold increase in loose bulk volume relative to the starting coal).

$$\text{Residue Loose Bulk Density} = \frac{\text{Residue Mass (g)}}{\text{Loose Bulk Volume (cc)}} \quad (1)$$

$$\text{Free Fall Swelling Index} = \text{FFSI} = \frac{\text{Residue Loose Bulk Volume (cc)}}{\text{Coal Loose Bulk Volume (cc)}} \quad (2)$$

The need to develop an alternative to conventional tests for thermoplastic tendency is made more clear by the data in Table 2, a comparison of ASTM Free Swelling Index (FSI) and the FFSI of selected coals determined under CCG conditions. The ASTM FSI's are all low, that is, there is no swelling and little or no agglomeration, but the FFSI's range from 1.0 to 5.6. There are also clear morphological differences in the residues from both tests. The FSI

residues are granular solids which retain the sharp edges and dull surfaces found in the original coal. But the free fall residues "B" and "C" are composed of bloated, reflective spheres which appear to have gone through a fluid stage (as in Figure 1). The thermoplasticity implied by the morphological differences between coal and pyrolyzed residue was later directly observed by capturing on film the behavior of rapidly heated single particles of catalyzed Illinois No. 6 coal in a fast photography cell (FILM SEGMENT #1: Illinois + 12.2 wt % KOH, 0.1 MPa helium, filament heat-up rate = 1000°K/sec). Melting, bubbling, swelling, and thermosetting were clearly evident.

The possibility that a coal could exhibit no swelling at low heat-up rate but exhibit distinct swelling at a higher heat-up rate is implied by the work of Van Krevelen^{2a}. Therefore, the contrasting FSI and FFSI results obtained here come as no surprise because of the large difference in heat-up rates (FSI = 5°K/sec, FFSI >1000°K/sec). Since the conditions of the Free Fall Swelling Test more nearly resemble CCG conditions, and because swelling behavior in the test is at least qualitatively more in line with behavior in a fluid bed gasifier, the Free Fall Swelling Test seemed to be the better choice to study thermoplasticity at CCG conditions.

Effect of Pressure

Thermoplastic behavior of potassium-catalyzed Illinois No. 6 coal was first observed in CCG work during large scale char preparation in a 0.78 MPa/3 kg-ks⁻¹ Fluid Bed Gasifier (FBG). Fluid bed densities which were lower than previously measured were noted in the FBG³. During start-up of the PDU with the same coal, feedline plugging caused by agglomeration was frequently a problem⁴. Fixed bed laboratory tests then identified pressure as one important variable in catalyzed coal agglomeration⁵. PDU runs also suggested the importance of pressure, and of oxidation, to fluid bed density^{1b}. However, since other variables such as superficial velocity changed along with pressure, it was difficult to uniquely determine the effect of pressure on thermoplasticity and gasifier properties.

The variation of the loose bulk density of pyrolyzed coal from the Free Fall Swelling Test with pressure (Figure 3) is in agreement with this earlier data which indicate that higher pressures increase coal thermoplasticity. The densities of uncatalyzed and catalyzed-oxidized Illinois No. 6 coals decrease as the Free Fall Unit pressure is raised above atmospheric pressure. Char densities at 3.5 MPa fall into the expected order: catalyzed-oxidized > catalyzed > uncatalyzed. The reproducibility of the measurement is indicated by good agreement between the two sets of data on catalyzed-oxidized coal (Figure 3, □ and Δ). The effect of pressure on thermoplasticity, as manifested by swelling, was later directly observed by fast photography of single particles of potassium catalyzed Illinois No. 6 coal (FILM SEGMENT #2: Illinois + 12.2 wt % KOH at 3.5 MPa). These films show more swelling at 3.5 MPa than at 0.1 MPa.

This trend is attributed to the effect of pressure on the volatile components during the extremely rapid pyrolysis. It is thought that higher pressure retards the escape of volatile pyrolyzates from coal particles by shifting the boiling points of the volatile components to a higher temperature range. Because of the short time involved with the rapid heating, most of the volatile components will remain in the particle until they begin to boil (i.e., their vapor pressure equals the total pressure of the system). With the more volatile and, hence, likely less viscous and solvent-like components retained to a higher temperature, the coal attains a lower viscosity during the plastic transition. Because of this lower viscosity, the evolving gas has a greater swelling effect on the unconstrained, free falling, plastic coal particle. At a pressure of approximately 1.5 MPa (200

psig), the majority of the components that will affect the viscosity of the particle appear to have been retained, for further increase of pressure has little effect on swelling (loose bulk density). Increased pressure is expected to reduce the total volume of pyrolysis gases released, but because the gas volume is still many times greater than the volume of the resulting char, increasing pressure from 1.5 to 5.5 MPa (200 to 800 psig, or decreasing the volume of the pyrolysis gases by a factor of four) should not have a large effect on swelling. If this line of thinking is extended, it would predict that swelling will begin to decrease at much higher pressures where the volume of the evolving gases is contracted severely (loose bulk density will increase).

Effect of Catalyst, Oxidation and Longer Particle Penetration Time

The effects of catalyst, oxidation, and longer penetration time on thermoplasticity, as measured by FFSI, are summarized for several coals of interest to CCG in Figures 4-7. These include Illinois No. 6, Valley Camp, and Hawk's Nest coals which are bituminous in rank, and Wyodak coal which is sub-bituminous in rank.

The effect of potassium catalyst is to reduce thermoplasticity whether the coal is purposely oxidized prior to catalyst addition or not (Figure 4). The exception is Wyodak coal which is very close to being non-swelling even without potassium catalyst. Decreased swelling upon catalyst addition is thought to be due to the factors of salt formation between the catalyst and the coal, and reduced pyrolysis.

Oxidation after catalyst addition reduces swelling for the more porous Illinois No. 6 (13 wt % equilibrium moisture, uncatalyzed) but does little for the much less porous Hawk's Nest coal (5 wt % equilibrium moisture, uncatalyzed; Figure 5). This suggests that oxygen has difficulty penetrating less porous particles.

Mild oxidation alone can reduce swelling without catalyst addition, and more extensive oxidation reduces swelling still further. However, the application of potassium catalyst after oxidation results in a large additional reduction of swelling, presumably because the aqueous application allows the catalyst to migrate to new surface acids formed during oxidation. This is demonstrated by lower FFSI's after additional penetration time is allowed the catalyst. The effect of poor catalyst dispersion is also discussed in the next section.

The sequence of increasing coal swelling after catalyst application and oxidation in preparation for PDU operation is, as shown in Figure 7, Wyodak (FFSI=1.0) < Illinois (FFSI=2.5-2.85) < Valley camp (FFSI=3.1) < Hawk's Nest (FFSI=3.6-4.5).

Effect of Catalyst Dispersion

Even when mixed with potassium catalyst in an aqueous slurry and given an extended soak at mild conditions, some coals such as Hawk's Nest coal do not take up the catalyst effectively. The catalyst lays down as a rim on the exterior of particles which can clearly be seen in Scanning Electron Microscope (SEM) photomicrographs of particle cross-sections. When heated in the fast photography cell, these particles exhibit two distinct thermal behaviors. The well-catalyzed outer rim does not melt on heating, but merely cracks. The poorly catalyzed particle interior does melt and flows out through the cracks in the unmelted outer rim (FILM SEGMENT #3: Hawk's Nest + 12.2 wt % KOH).

Effect of Atmosphere

The effect of selected inert and reactive gases on residue loose bulk density was examined because there are a variety of gases in a CCG atmosphere which may have different effects on thermoplasticity. Other work has shown that the nature of the gas atmosphere does affect thermoplasticity at pressure as measured by maximum fluidity in a plastometer⁶. In the Free Fall Swelling Test, it was found that H₂, He, CO₂, Ar, and N₂ gave residues with densities which spanned a range of only 0.02 g/cc (Figure 8). The cause of this small difference is thought to be the speed with which pyrolysis takes place in the Free Fall Swelling Test. Under conditions of rapid pyrolysis, it may be possible for particles to become blanketed in an atmosphere of their own pyrolyzates which isolates the particles from the bulk atmosphere. If some additional conversion does occur in reactive gases (H₂, CO₂), then densification must occur at the same time in order for the coke densities to be so similar.

Summary

We have found the Free Fall Swelling Test to be helpful in the guidance of pilot plant work and in determining the effect of several CCG variables on thermoplasticity. Under the test conditions of high pressure and high heat-up rate, the coal thermoplastic property is more pronounced than at conditions of low heat-up rate and low pressure under which more conventional tests for thermoplasticity are run. Thus, the test is a more sensitive probe of the thermoplastic tendency, especially for coals having a limited thermoplastic tendency.

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TABLE 1
CHARACTERISTICS OF PDU FEED COALS (UNCATALYZED)

	Illinois No. 6 (Monterey No. 1)	Hawk's Nest	Valley Camp	Walden	Wyodak
Coal Rank	Bituminous	Bituminous	Bituminous	Bituminous	Sub-bituminous
Equilibrium Moisture (Wt %)	13.4	5.1	7.4	9.5	28.7
Free Swelling Index	4	3	2	0.5	0
Ultimate Analysis (Wt % Dry Coal)					
Carbon	69.4	75.6	73.3	69.6	67.0
Hydrogen	4.8	5.4	5.6	4.8	5.2
Oxygen (Difference)	8.9	10.2	11.7	12.6	15.3
Nitrogen	1.4	1.7	1.4	1.3	1.0
Sulfur, Total	4.6	0.5	0.7	0.6	1.0
Pyritic	0.8	0.1	0.2	0.3	0.2
Sulfate	0.1	0.0	0.0	0.0	0.2
Organic	3.8	0.4	0.5	0.3	0.7
Chlorine	0.2	0.1	0.0	0.0	0.0
Ash Elements (SO ₃ -Free, % Ash, Dry)					
SiO ₂	51.0	51.1	60.0	54.5	40.6
Al ₂ O ₃	18.4	23.9	11.3	29.0	22.7
P ₂ O ₅	0.4	0.9	0.3	1.0	1.2
TiO ₂	1.1	1.1	1.0	0.7	1.7
Fe ₂ O ₃	19.8	10.7	7.4	5.0	6.0
CaO	4.9	7.8	16.2	8.0	21.2
MgO	1.0	2.0	2.4	0.8	5.2
K ₂ O	2.1	1.4	1.2	0.3	0.5
Na ₂ O	1.4	1.1	0.3	0.8	0.9

Table 2
ASTM Free Swelling Index (FSI) and Free Fall Swelling Index (FFSI)
of Selected CCG Coals

Coal	ASTM FSI	FFSI (a)	Free Fall Residue Density, g/cc
A Wyodak + K	0.0 (no swelling)	1.0	0.37
B Illinois No. 6 + K (oxid.)	0.0 (no swelling)	2.6	0.15
C Illinois No. 6 + K (unox.)	0.5 (no swelling)	5.6	0.09

(a) FFSI conditions were 978°K and 3.5 MPa.

FIGURE 1

SOME CATALYZED BITUMINOUS COALS EXHIBIT UNDESIRABLE THERMOPLASTIC BEHAVIOR WHEN FED TO A FLUID BED GASIFIER

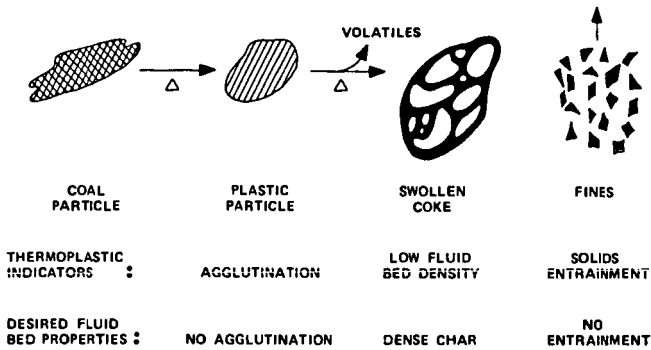


FIGURE 2

FREE FALL UNIT SCHEMATIC

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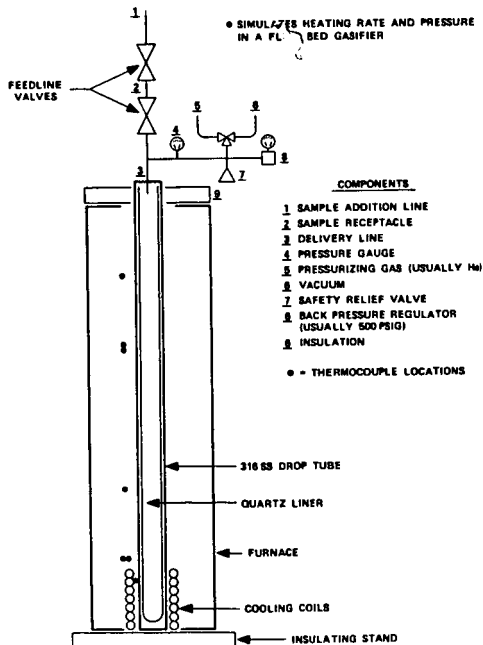
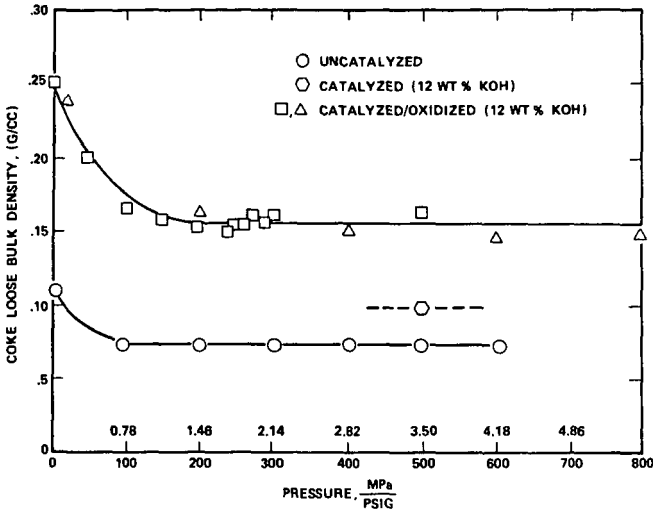


FIGURE 3

INCREASED PRESSURE DECREASES ILLINOIS CHAR DENSITY

- HELIUM ATMOSPHERE
- 1033°K
- ILLINOIS NO. 6 COAL



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FIGURE 4

CATALYST REDUCES THERMOPLASTIC SWELLING

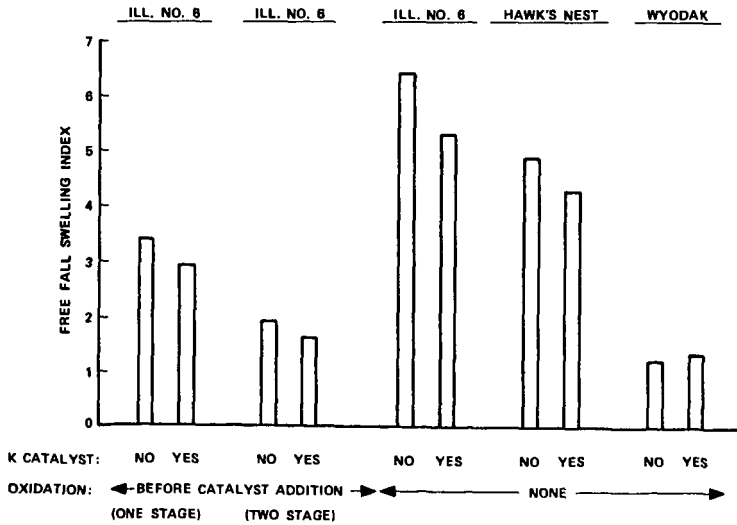
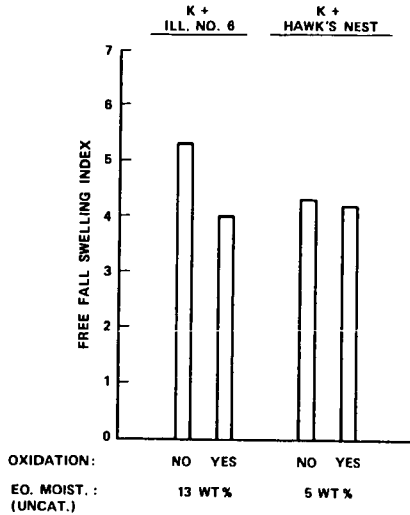


FIGURE 5

OXIDATION REDUCES SWELLING OF THE MORE POROUS COAL



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FIGURE 6

WHILE OXIDATION ALONE HAS AN EFFECT, CATALYST APPLICATION AND INCREASED PARTICLE PENETRATION TIME RESULT IN AN ADDITIONAL REDUCTION OF SWELLING

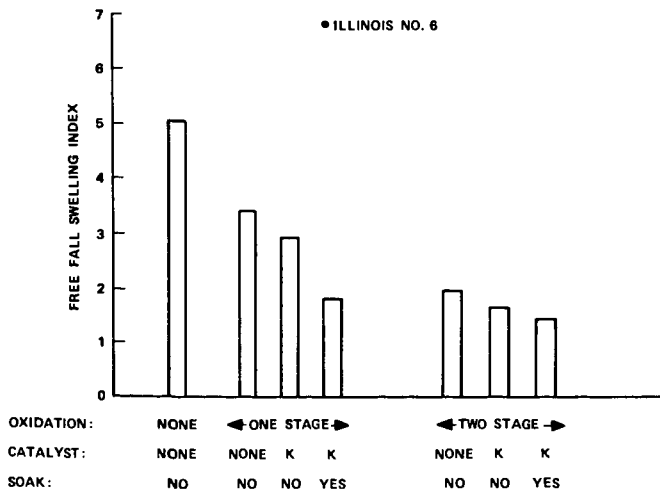


FIGURE 7
THERMOPLASTIC SWELLING OF CCG COALS VARIES

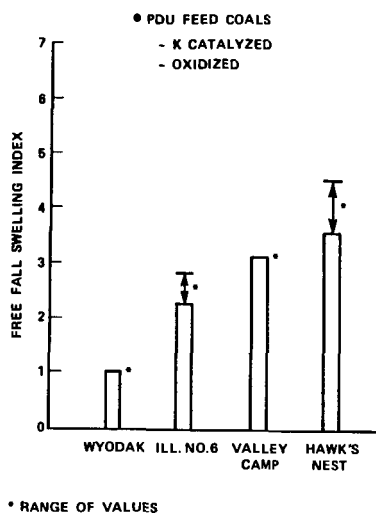
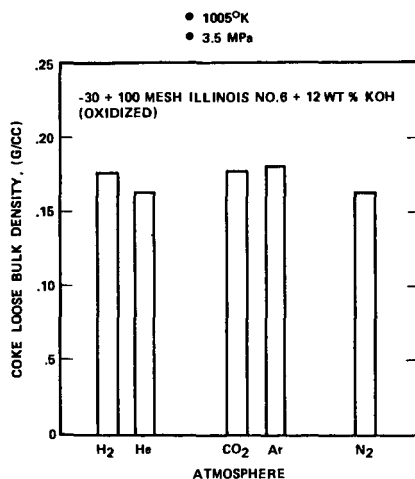


FIGURE 8
ATMOSPHERIC EFFECTS ON RESIDUE LOOSE BULK DENSITY
ARE SMALL AT HIGH PRESSURE



PRODUCTION AND GASIFICATION TESTS OF COAL FINES/COAL TAR EXTRUDATE

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ABSTRACT

Fixed bed gasifiers, such as those planned to be used to manufacture SNG commercially, require a sized feedstock, e.g., -2 in., $+1/4$ in. As an alternative to disposing the fines ($-1/4$ in.) which cannot be used in the boiler of such an SNG plant, they can be compacted and then fed to the gasifiers. General Electric R&D Center in Schenectady is developing an extrusion process which will enable the fines, mixed with an appropriate binder, to be fed directly into a fixed bed gasifier, bypassing the lockhoppers required for lump coal feed. Work is described on a recently completed extrudate manufacture and gasification program sponsored by GRI. GE's 6-inch diameter, single screw extruder was employed to produce the extrudate from Illinois No. 6 coal and coal tar, and the extrudate was subsequently gasified in GE's pressurized air-blown, stirred fixed-bed reactor. The test results indicate that the extrudate makes a satisfactory gasifier feedstock in terms of both thermal and mechanical performance.

INTRODUCTION

Gasification is a fuels conversion technology which permits the production of clean substitute gas from coal and other carbonaceous fuels. The first commercial application of this technology in the U.S. will be the Great Plains substitute natural gas (SNG) plant, which is due to begin production in late 1984. This plant will produce 125M SCF per day of pipeline quality gas using Lurgi, oxygen blown, fixed-bed gasifiers.

While the fixed bed gasifier offers proven performance in terms of both thermal efficiency and reliability, it requires a sized feedstock for optimum performance. Typically, coal below 1/4 inch is removed by screening prior to gasification in order to minimize fines carryover from the bed and to minimize instabilities in gasifier performance caused by excessive fines content in the feed. Run-of-mine (ROM) coal, however, typically contains 25-35% of <1/4-inch material, which means that up to 35% of the coal mined could not be utilized directly in the gasifier. Direct extrusion of the coal fines fraction with a tar binder offers a potentially attractive solution to this problem by consolidating the fines into a feedstock suitable for the fixed-bed gasifier and, at the same time, providing an advanced feed mechanism to the pressurized reactor.

The present paper describes the results of a recently completed extrudate evaluation program conducted at the General Electric Research and Development Center in Schenectady New York, under the joint sponsorship of the Gas Research Institute (GRI) and the New York State Energy Research and Development Authority (NYSERDA). A six-inch single screw extruder previously developed by General Electric was used to produce 88 tons of Illinois No. 6 coal extrudate using a 15% coal-tar pitch binder (Ref. 1). The extrudate was then successfully gasified in General Electric's 1 ton/hr, Process Evaluation Facility (PEF) scale, pressurized fixed-bed gasification system. Data is presented on gasifier performance, fines carryover rate, and tar yields from the extrudate. Performance data on the extrusion process is also included.

EXTRUSION TRIALS

General Process Description

General Electric began development of the coal extruder system in response to industry's need for an improved coal feed system and as a means of utilizing fines in a pressurized fixed-bed reactor. The work was initiated on a 1-inch extruder and progressed to the development of a 6-inch diameter single screw extruder capable of processing in excess of one ton per hour of coal against backpressures up to 350 psig. The later work was done under the sponsorship of EPRI (Project No. 357-1).

The extruder process is shown schematically in Figure 1. Coal under 1/4- inch is mixed with a binder, typically coal tar, in a heated mixer and then conveyed to a screw extruder where it is simultaneously compacted and forced into the pressurized reactor. Proper design and control of the die at the delivery end of the extruder maintains a gas seal and adjusts the frictional resistance of the compacted coal to forward motion. The extrudate exits the die as a solid log of coal which is subsequently broken up by a chopper inside the reactor.

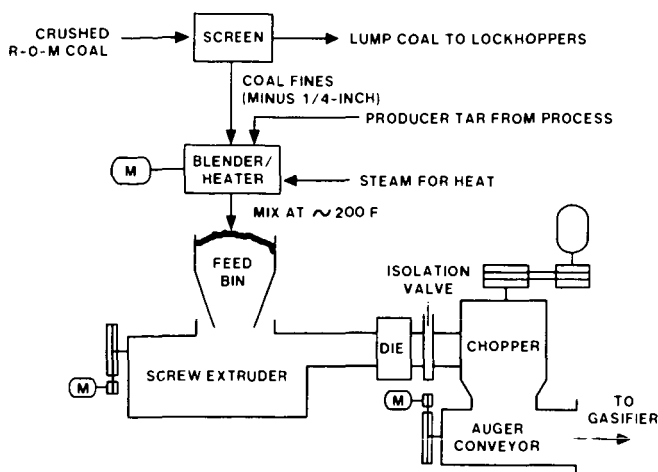


Figure 1. Coal Extrusion Process

The General Electric extruder is driven by a 60 hp variable speed drive which permits screw speed to be varied from 0-45 rpm. Screw construction is segmented with individual auger sections stacked along a central drive shaft to give a continuous worm. The auger sections are cast from high chrome steel having a Rc 60-67 hardness to minimize wear. The length-to-diameter ratio of the machine is 4:1. The barrel is made up of two steam-jacketed sections, each equipped with a hardened and ribbed steel liner. Two counter-rotating packer wheels are used in the feed hopper to help promote flow of the preheated extrudate mix into the screw cavity. Extrudate formation is controlled by a patented variable area, variable length die which permits on-line control of extrudate density. This feature has been found essential for permitting stable operation of the extruder over a range of operating conditions and on a variety of feedstocks. Power consumption and machine wear are also minimized.

Steam-jacketed, 15 ft³ scale-mounted paddle mixers were used to prepare the hot (150-175F) coal-tar extrudate blends. Milled coal was supplied to the mixer via a fines elevator. The coal was prepared for testing by hammermilling stoker grade Illinois No. 6 coal through a nominal 4-mesh screen. A screen analysis of the coal taken after crushing indicated a size distribution nearly identical to that of coal fines obtained from underscreened ROM coal. The coal was not dried prior to size reduction. Typical mix times for a 400 lb test batch were 12-15 minutes.

Mix Evaluation

Several different tar binder-coal combinations were evaluated prior to the start of production to arrive at a mix which extruded well and which possessed sufficient mechanical strength to withstand the handling and bed forces encountered during a gasification test. A total of 17,000 pounds of material was processed using seven different tars at varying weight percentages with Illinois No. 6 coal.

A list of the binders tested is shown in Table 1. All are coke oven derivatives with the exception of the asphalt pitch, and represent a commercially available range of softening points from slightly above room temperature to almost 200°F. Producer tars from actual gasification plants were not included in the study due to the lack of availability of these tars in sufficient quantities.

Table 1
TAR BINDERS TESTED

Tar Supplier	Designation	Softening Point ^a
General Electric	V-1 PEF gasifier tar	<40°C ^b
Koppers	Medium-soft coke oven	50-55°C
Koppers	Medium coke oven pitch	56-64°C
Reilly	No. 12 coke oven tar ^c	<50°C)
Reilly	Medium coke oven pitch	54-62°C
Reilly	Hard coke oven pitch	82-95°C
—	Canadian Asphalt pitch	

^aring and ball

^bestimated

^cselected for production run

Reilly No. 12 coal tar pitch was chosen as the test binder, based on its satisfactory performance in the extruder, its commercial availability, and the satisfactory mechanical properties of the extrudate obtained. The relatively low softening point of this tar also more closely approximated that of the raw tar which would be obtained from an actual gasification plant. A blend of 15% tar, 85% coal by weight was selected for the final production run. The use of this low softening point binder required modifications to be made to the mix preparation system to allow consistent production of extrudate with adequate green strength. This entailed lowering the mixer jacket temperature from 350°F to 190°F, and installation of a tempering water spray just upstream of the extruder inlet to further cool the extrudate mix. With this configuration, mixes of <120°F could be consistently produced, which was sufficiently low to allow production of good quality extrudate.

Extrudate Production

Approximately 88 tons of extrudate were produced offline in the 6-inch extruder over a 9-day operational period. The continuous 6 1/2-inch diameter logs were cut manually into 2-ft lengths, allowed to cool for approximately 2 to 4 hours, then crushed to <1 1/2-inches in a rotary crusher. The resultant extrudate was screened to remove any fines generated during size reduction and stored for testing.

Excellent performance was obtained from the extrusion system throughout the test period. On-line availability of both the mix preparation and extruder exceeded 98% and wear on machine parts including the auger was negligible. Specific power consumption of the extruder was exceptionally low and control over extrudate formation was good once stable operation had been achieved. A summary of the extruder operating conditions is shown in Table 2.

Table 2
PRODUCTION RUN SUMMARY —
EXTRUDER OPERATING CONDITIONS

Machine	6 in. single screw
Die	6.5 in. i.d., adjustable
Auger	3 in. pitch, segmented
Mixture	85% Ill. No. 6, 15% Reilly tar
Total production	175, 500 lbs.
Throughput	1305 lb/hr.
Specific power	1.5 hp-hr/ton
Shaft speed	12 RPM
Die length	4 in.
Flap pressure	150-200 psig
Auger wear	Negligible
Barrel temp	Cooling water on
Control	Excellent

Extrudate Properties

Laboratory evaluations were performed to determine the mechanical properties of the extrudate. Tests run included a crush test to measure the mechanical strength of the extrudate before and after carbonization, a 1000°F oven test to determine the high temperature behavior of the samples, a softening point test to determine at what temperature the extrudate begins to soften, and a standard test to determine extrudate density. The results of the mechanical tests, which are summarized in Table 3, indicated that the extrudate should possess sufficient mechanical strength to withstand the gasification environment. These observations were later verified during the fired gasification trials.

Table 3
EXTRUDATE PROPERTIES

Mixture, wt%	85% Illinois No. 6, 15% Reilly No. 12 tar
Compressive strength, psi	810
Carbonized strength, psi	834
Density, lb/ft ³	72
Softening point, ^a T°F	130
Oven test results	Some swelling and distortion

^aPoint at which extrudate can be deformed by hand

GASIFICATION TRIALS

Gasification Facility

The General Electric Process Evaluation Facility (PEF), located in Schenectady, New York, consists of an advanced fixed-bed reactor, full-flow, low-temperature gas cleanup system, coal extrusion feed system, and an advanced computerized data acquisition, analysis and control system. The facility operates at a nominal pressure of 20 atm. and can gasify approximately 1 ton of feedstock per hour using air and steam as reactants. Deep bed stirring provides the capability for the gasifier to operate on caking coals and at thermodynamically attractive low steam-air ratios. The raw fuel gas is conditioned in a two stage cleanup system which removes solid particulates, hydrocarbon mist, and sulfur compounds from the gas stream. A schematic of the PEF is shown in Figure 2, and the gasifier is shown in cutaway side-section in Figure 3.

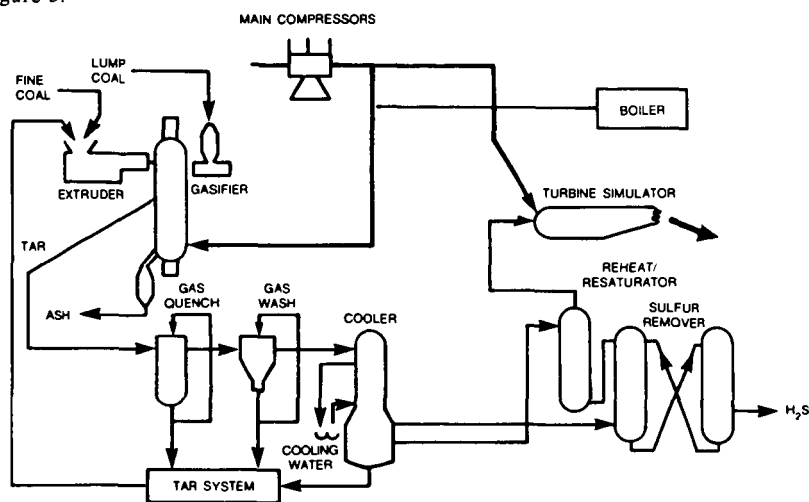


Figure 2. Process Evaluation Facility

Gasifier Performance

Approximately 50 tons of Illinois No. 6-Reilly No. 12 extrudate were successfully gasified in the PEF during a 50 hour operational test period in July, 1983. The gasifier was operated at steady-state, full pressure, full flow design conditions for the duration of the test run. The average gasifier operating conditions for a representative 20-hour time period are presented in Table 4. Ultimate and proximate analyses of the extrudate feedstock appear in Table 5.

Performance parameters characterizing the operation and efficiency of the gasifier were determined for the representative test period. These parameters are presented in Table 6 along with average results from previous baseline testing on Illinois No. 6 lump coal (Ref. 2).

The efficiency of gasification is quantified by the carbon, cold gas, and steam utilization efficiencies. The carbon efficiency provides an indication of the amount of input carbon which is converted to gaseous form in the tar and oil-free product gas. The cold gas efficiency

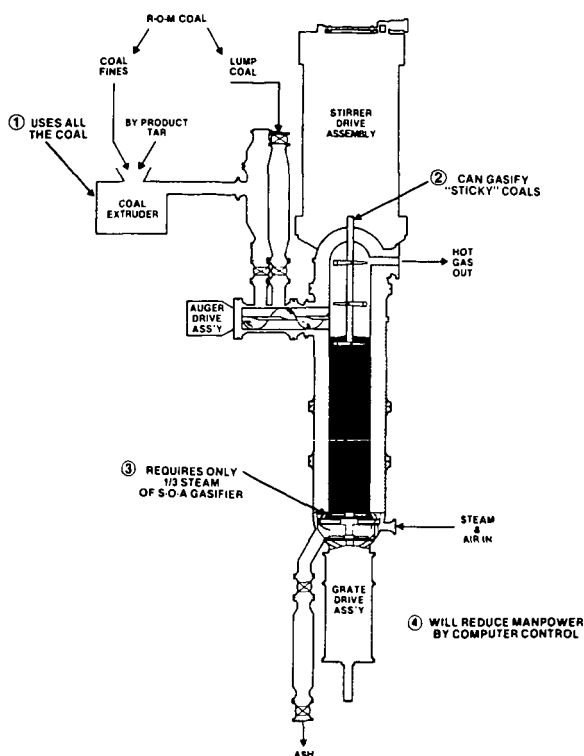


Figure 3. Advanced Fixed Bed Gasifier

Table 4
AVERAGE GASIFIER OPERATING CONDITIONS

Extrudate flow, lb/hr	1925
Air flow rate, lb/s	1.20
Steam flow rate, lb/s	0.48
Steam-to-air, lb/lb	0.40
Blast temperature, °F	363
Hot gas temperature, °F	1040
Vessel pressure, psig	300
Bed level, ft	10.7
Stirrer cycle	
raise, ft/min	1.0
lower, ft/min	0.5
Dry ash removal, lb/hr	176
Sludge removal, lb/hr	90

Table 5
EXTRUDATE ANALYSIS

	As Received	Dry Basis
Proximate Analysis (wt%)		
Moisture	7.60	—
Ash	9.12	9.90
Volatile	34.92	37.80
Fixed Carbon	48.37	52.30
Sulfur	1.34	1.45
Ultimate Analysis (wt%)		
Moisture	7.60	—
Carbon	69.11	74.78
Hydrogen	4.68	5.06
Nitrogen	1.55	1.68
Chlorine	0.11	0.12
Sulfur	1.34	1.46
Ash	9.12	9.90
Oxygen (difference)	6.48	7.01
Metals (wt% in dry ash)		
Sodium		0.35
Potassium		1.71
Iron		10.50
Calcium		2.75
Heating Value (Btu/lbm)	12342	13354
Moisture and Ash Free	—	14822
Free Swelling Index	3.9	

is defined as the higher heating value of the tar and oil-free raw gas at 60°F divided by the extrudate heating value. The steam utilization represents the percentage of the blast steam that takes part in the gasification reactions.

The carbon utilization of 83.5% for the extrudate run indicates good conversion of carbon to fuel gas heating value. The value is slightly lower than that obtained on Illinois No. 6 lump coal, primarily due to the higher condensable hydrocarbon content in the extrudate-produced gas. The higher tars and oils content also resulted in a slightly lower cold gas efficiency than determined for the lump coal. If the heating value of these tars is included, the calculated cold gas and carbon efficiencies would result in slightly higher values for the extrudate feedstock. The steam utilization value is excellent and nearly identical for both feedstocks, indicating good fuel reactivity and good gas-solids contact in the fuel bed.

The gas composition was similar for both fuels, the only detectable difference being a slightly lower methane content and slightly higher CO₂ level for the extrudate case. The overall dry gas heating value of 162 Btu/scf for the extrudate-produced fuel is satisfactory and compares favorably with results obtained from stoker grade lump coal.

Table 6
PERFORMANCE PARAMETERS COMPARISON

Performance Parameter	Extrudate Feedstock	Illinois No. 6 Lump Coal
Carbon utilization, %	83.5	86.0
Steam utilization,	55.7	56.0
Cold gas efficiency, %	71.2	74.7
Gas composition, vol%	64.7	68.0
H ₂	21.0	21.0
CO	17.1	17.1
CO ₂	13.2	12.8
N ₂	43.8	43.9
CH ₄	4.0	4.4
H ₂ S	0.3	0.3
Dry gas heating value, Btu/scf	162	166
Tar yield, wt% dry coal	7.8	4.0
Dry fines carryover, wt% dry coal	2.1	3.6

The dry fines carryover represents the percentage of feedstock carried over from the fuel bed to the quench vessel. The relatively low dry fines carryover value for the extrudate testing indicates that the extrudate maintained its integrity in the fuel bed during gasification. This result is particularly significant considering that the extrudate is produced from essentially 100% fines.

The gasifier exhibited excellent mechanical performance throughout the extrudate run. No major problems with extrudate feeding, bed conditioning, or ash discharging were experienced during the test. The peak rotational torque loadings on the stirrer and grate paddle were 3,400 and 14,000 ft-lbs, respectively, and were safely below the design limit values. In general, the mechanical performance of the gasifier on the extrudate feedstock was very similar to that experienced during operation on lump coals.

Gas Cleanup System Performance

The gas cleanup system was operated at steady design conditions for the duration of the extrudate test run. All of the cleanup components functioned smoothly, indicating no specific problems associated with the extrudate-produced fuel gas. Results from the particulate sampling indicate that the overall cleanup system particulate removal efficiency was nearly 99%, typical of that seen on lump coal.

Comparative tar collection data is presented in Table 7 for both the extrudate and lump coal runs. The total tar collection rate obtained from the cleanup system components on extrudate was approximately double that obtained during Illinois No. 6 lump coal runs. This higher tar yield can be attributed primarily to carryover of vaporized extrudate binder, which,

when added to the normal tar carryover from the volatile matter in the base coal, yields the rates shown. However, although the total rate is nearly double, it is only approximately 25% of that which would be obtained if all the binder appeared in the raw gas. This translates to an apparent cracking rate of 75% of the extrudate binder during a single pass through the gasifier.

Table 7
TAR CARRYOVER COMPARISON

	Extrudate Feedstock	Illinois No. 6 Lump Coal
Tar Collection Rate, lb/hr	117.7	57.0
Tar Yield, Wt. % Dry Coal	7.8	4.0

SUMMARY

The results of the test program indicate that Illinois No. 6-Reilly No. 12 extrudate makes an attractive feedstock for fixed-bed gasifiers in terms of both fines and tar utilization, as well as overall gasifier performance. Fines carryover was reduced from a typical value of 3 — 4% on lump coal to 2% on extrudate, a result which is particularly significant considering the extrudate is produced from essentially 100% fines. Approximately 75% of the tar binder cracked during the first pass through the gasification process. The cold gas efficiency of 71% and fuel heating value of 162 Btu/scf were comparable to results obtained on Illinois No. 6 lump coal. The mechanical performance of the reactor was also satisfactory.

The 6-inch coal extruder performed well throughout the program. Power consumption was low (1.6 kwh/ton), machine wear was negligible, and reliability excellent. Power consumption and wear would be expected to be somewhat higher under on-line extrusion conditions due to the need to maintain a gas seal in the die area. Accurate temperature control of the mix was found to be a critical variable in producing extrudate with adequate green strength when using a low softening point binder such as Reilly No. 12 tar.

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PYROLYSIS AND HYDROPYROLYSIS OF COAL ASPHALTENES.

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Coal asphaltenes and their behaviour under typical coal liquefaction conditions have attracted considerable attention in recent years (1, and references therein), because of both their proposed role as intermediates in liquefaction processes and the potential problems presented by incomplete conversion of asphaltenes. The present work extends our previous studies on asphaltene fractions from coal extracts (1,2) to permit comparisons to be drawn between two asphaltenes, each derived from a hydrogenated-anthracene-oil extract of bituminous coal, but having significantly different carbon and oxygen contents.

Experimental.

The coal extract used was kindly supplied by the Coal Research Establishment, National Coal Board, Cheltenham, England. It was derived from Point of Ayr coal, extracted by a hydrogenated anthracene oil (Veba Oil).

Cylinder gases were obtained from the British Oxygen Company, and CoO-MoO₃ on AlO₃ from Strem Chemicals Inc. Details of the isolation of asphaltenes, by extraction into benzene followed by precipitation using n-pentane, are given elsewhere (1).

Pyrolysis and Hydropyrolysis Procedure.

Reactions were carried out in the stainless steel autoclave of 250 ml volume described previously (1), which was charged with asphaltene (1.5g) finely ground with catalyst (CoO-MoO₃ on AlO₃, 0.15g). After closure, the bomb was pressured to 87 bar (1300 p.s.i.) cold pressure with the appropriate gas (oxygen-free nitrogen for pyrolysis experiments, hydrogen for hydropyrolysis experiments). The temperature profiles of the reactions were complicated due to the considerable thermal mass of the bomb, and heat-up times varied between 40 mins. (to 200°C) and 60 mins. (to 425°C). Nominal reaction times are given as the number of minutes at the designated temperature, ignoring heat-up and cooling.

Fractionation of Products.

After cooling overnight, the bomb pressure was released by using a specially adapted two-stage needle-valve to leak the gases slowly into a train of three pre-weighed stainless-steel U-tubes loosely packed with dry molecular sieve (1/16in. pellets, type 3A), maintained at liquid nitrogen temperature. After reweighing, the traps were warmed to room temperature and the evaporating gases were transferred to an evacuated glass bulb fitted with a rubber septum to allow withdrawal of samples, using a gas-tight syringe, for injection onto a g.c. column. Following this out-gassing, the bomb was opened, benzene (20 ml) was added and the resulting slurry was coated onto cleaned glass beads (100-200 mesh, 100g) which were successively extracted, according to the method of Awadalla et al.(3), with n-pentane, benzene and pyridine. The bulked n-pentane solution was reduced in volume on a rotary evaporator to ca 20 mls weighed, then a 8µl

sample was withdrawn and injected onto the capillary g.c. column. The percentage of solvent (n-pentane and benzene) present was estimated from the g.c. trace and in this manner an approximate weight was arrived at for the n-pentane soluble product. The method was devised to minimise the under-estimation of light constituents such as methylated benzenes, which is inherent in any total drying of this fraction. The benzene and pyridine were removed from the asphaltene and preasphaltene solutions respectively, using a rotary evaporator and these products were dried in a vacuum oven (60°C , 3 hr) before weighing.

Analytical Procedures.

Elemental analyses were carried out by the University of Strathclyde Microanalytical Service. ^1H -n.m.r. spectra were recorded in deuteriochloroform at 100 MHz on a Jeol MH100 spectrometer and (^1H) - ^{13}C -n.m.r. spectra in deuteriochloroform at 50MHz using inverse-gated decoupling with a 10 sec. delay, and 100mg chromium acetylacetonate added to the sample.

Characterisation of gaseous products was carried out using a Hewlett-Packard model 5880A gas chromatograph fitted with a 2m, 3.2mm OD stainless-steel column packed with Porapak Q, and an oven temperature of 160°C . Nitrogen carrier gas and a flame ionisation detector were used, permitting identification of hydrocarbon gases only. No attempt was made to detect fixed gases. For the pentane-soluble products, a 50 m open tubular capillary column (fused silica with SE54 silicone gum as stationary phase) was used, with the oven temperature programmed from 50 – 265°C at $5^{\circ}\text{C min}^{-1}$ holding for 48 min. at 265°C . Further identification of the pentane-soluble material was carried out at the Institute of Offshore Engineering, Heriot-Watt University, using computerised g.c. - mass spectrometry with an INCOS data system. Samples were injected onto a 25m OV-101 fused silica column with the oven programmed from 50 – 260°C at $5^{\circ}\text{C min}^{-1}$, holding at 260°C for 48 min.

Pyrolysis Experiments.

Following our earlier work (1) on an asphaltene (A) with carbon content of over 91% and carbon aromaticity of 80%, we have carried out a series of experiments using a second asphaltene (B), with 87.1% carbon and 74% carbon aromaticity. Pyrolysis and hydropyrolysis reactions were carried out, to allow comparisons with the previous study on asphaltene A.

Pyrolysis at 425°C of asphaltene B in a mini-bomb reaction vessel (1) gave a product (see Table 2) consisting largely of asphaltene and pre-asphaltene (total 78%) with 9% n-pentane soluble material and 8% pyridine-insoluble material ("coke"). This compares with a rather higher coke content (23%) and a low percentage of n-pentane soluble material (3–4%) in the product from asphaltene A, confirming the expectation that the asphaltene of lower carbon content and aromaticity would give rise to more tractable products. However, the results of this kind of pyrolysis experiment are extremely sensitive to changes in the conditions of the reaction. Thus, when asphaltene B was pyrolysed at 425°C in the Parr bomb under nitrogen pressure, in conditions of geometry and pressure

mimicking those used in the hydrogenation studies, a quite different product was obtained, consisting largely of gases (defined as C_1-C_4 hydrocarbons plus H_2S and other minor constituents) and coke. Only 6% was recovered as asphaltene or preasphaltene. Clearly, the changes in geometry, pressure and true reaction time combined to produce a result quite different from that obtained in the mini-bomb. Bearing this in mind, the data from the Parr bomb pyrolyses are used below as the basis for comparisons with hydropyrolysis experiments.

Hydropyrolysis Experiments.

Pyrolysis at $425^\circ C$ of asphaltene B under hydrogen pressure in the presence of a hydrogenation catalyst gave product distributions shown in Fig. 1. Even at the shortest reaction time (10 min) conversion to over 40% pentane-soluble material was achieved, with less than 20% recovery of asphaltene. After 1 hour at $425^\circ C$, only 12% asphaltene was recovered while the pentane-soluble yield was maintained at $> 40\%$. However, the conversion to gas in the latter case was higher than at the shorter reaction time, the level of preasphaltenes and heavier products remaining low. This compares with much lower conversion of asphaltene A under identical conditions (see Fig. 2), accompanied by larger amounts of preasphaltene and coke. In general, for both asphaltenes, pyrolysis under nitrogen led to gas and heavy preasphaltenes and cokes as the major products - a result that can be regarded as a disproportionation of the starting asphaltene. Similar reactions under hydrogen pressure led to increased recovery of liquids and asphaltene, suggesting stabilisation of reactive fragments by hydrogen, but significant amounts of gas were still generated, particularly from asphaltene A, at longer reaction times.

Product Analysis.

Elemental analysis and ^{13}C -n.m.r. spectroscopy (see Table 1) revealed no significant differences in carbon content or carbon aromaticity between starting asphaltene and recovered asphaltene in any of the reactions using asphaltene A. There was, however, an increase in aromaticity, as measured from 1H n.m.r. spectra, of 5% in hydropyrolysis and 9% in pyrolysis. A smaller increase (2% and 4% respectively) in hydrogen aromaticity was observed in the product asphaltene from the more reactive asphaltene B. This presumably reflects the pyrolytic loss, under all the conditions studied, of aliphatic structures present in the parent asphaltene and is reflected in the aliphatic content of the n-pentane soluble liquid products. The overall hydrogen/carbon ratio is also reduced in both asphaltenes recovered from pyrolysis, confirming the pyrolytic loss of hydrogen-rich material.

Differential Pulse Voltammetry [D.P.V.] (4) and Size Exclusion Chromatography [S.E.C.] on asphaltene B and its hydropyrolysis products indicate a slight shift to lower values for the molecular-weight distribution of the asphaltene recovered after reaction compared with asphaltene B itself. This is accompanied by a marked decrease in the D.P.V. peaks assigned to pyrene, anthracene and other polyaromatic structures, which can be characterised by D.P.V. even when substituted and linked together in larger molecules. Diaromatics such as naphthalene remain very much in evidence, however (5). Taken together with the n.m.r. spectroscopic evidence, this suggests that hydrogenation leads to a loss of purely aliphatic side-chains and partial hydrogenation of large polyaromatic structures to leave an asphaltene consisting largely

of diaromatic and monoaromatic centres (the latter not observable by D.P.V.) linked by methylenic bridges that constitute most of the remaining aliphatic character.

A detailed analysis of the composition of the n-pentane soluble products was carried out using gas chromatography-mass spectrometry. We have discussed previously (1,2) the identification in the asphaltene A products of a series of n-alkanes ranging up to C_{29} in the pyrolysis case, and to C_{14} in the hydropyrolysis case. A similar series of n-alkanes was found in the asphaltene B liquid products, together with a range of branched alkanes including traces of isoprenoids such as pristane (C_{17}) and phytane (C_{18}). Altogether the aliphatics (separated by column chromatography, see ref. 6) made up approximately 10% by weight of the B hydrophrolystate. A similar spectrum of aliphatic material was identified in the pyrolysate produced under nitrogen, supporting the suggestion that the majority of the alkanes originate as primary pyrolysis products. The remaining 90% of the liquid product is made up of aromatic hydrocarbons together with a trace (>2%) of polar materials, predominantly alkyl phenols and indoles. No sulphur-containing species has been identified in the liquid product, and most of the sulphur appears to be converted to H_2S .

The composition of the aromatic hydrocarbons that form the bulk of the liquid product - and hence some 40% of the total products - is of interest and has been analysed in some detail. Phenanthrene, pyrene and anthracene peaks are prominent in the D.P.V. trace of the pentane-soluble hydropyrolysate (5) and gas chromatography confirms that the single largest component in the mixture is phenanthrene which, together with other polyaromatics such as pyrene and fluoranthene, dominates the liquid product. This is qualitatively in accord with thermodynamic predictions (7). Both the pyrolysate and hydropyrolysate also contain a wide range of alkyl-benzenes, which may therefore be primary pyrolysis products, and a significant amount of dibenzofuran, possibly formed by condensation of neighbouring phenolic functions. The low level of phenolic material in the pentane-soluble fraction even of the pyrolysate was surprising in the light of earlier results (1) and the fate of the oxygen, phenolic and non-phenolic, requires further study. The hydropyrolysate also contains a range of partially hydrogenated polyaromatics arising from the fully condensed forms produced by pyrolysis. Phenanthrene and pyrene, in particular, are present in association with several hydrogenated forms in sufficient amounts to allow quantitation from capillary g.c. traces (see Figs. 3,4). Comparison of these results with "model-compound" studies of phenanthrene and pyrene hydrogenation (5,6) shows that, in the complex matrix present during asphaltene hydrogenation, the formation of perhydro-species is completely suppressed. Indeed, dihydrophenanthrene and dihydropyrene are the dominant hydrogenated species even at long reaction times. It is hard to envisage complete hydrogenation of these polyaromatic species under any realistic time-temperature-pressure regime. This is partly attributable to the tendency of some of the hydrogenated species to act as hydrogen donors, so that the asphaltene matrix becomes, as it were, a "hydrogen sink", inhibiting stepwise progress along a hydrogenation pathway. We have also found, and confirmed in separate pyrene studies (10) under similar conditions, that at the temperatures we have used a significant amount of pyrene breaks down, presumably via the 1,2-dihydro-form, to 4,5-dimethylphenanthrene which resists further hydrogenation. The character of the pentane-soluble pyrolysate and hydropyrolysate derived from asphaltene A does not differ greatly from that discussed here.

Further hydrogenation studies currently in progress will allow us to build up a more complete picture of the factors at work in asphaltene hydrogenation. However, we can summarise our conclusions to date as follows:

1. The general pattern of asphaltene conversion, viz., to gas and heavy, intractable materials on pyrolysis and to gas and liquids under hydropyrolysis conditions, remains the same for both average and high-carbon asphaltenes, but the extent of conversion to liquids upon hydropyrolysis is limited when the carbon content is high.
2. The aliphatic content of the liquids formed is low, not exceeding 10%, and arises from aliphatic groups present in the reactant asphaltene. The aliphatic content in the asphaltenes recovered after reaction is probably largely in the form of bridging methylenic functions.
3. The distribution of hydrogenated species in the highly aromatic liquid products indicates that complete hydrogenation of the polyaromatics produced in pyrolysis is difficult in the presence of a complex, hydrogen-hungry matrix. Conclusions drawn from model compound studies, while useful, must be used with caution in interpreting or predicting the behaviour of coal-derived materials.

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Table 1 : Analytical and Spectroscopic Data for
Various Coal-Derived Asphaltenes.

	Starting Material		Recovered from Pyrolysis		Recovered from Hydropyrolysis	
	A	B	A	B	A	B
% C	91.9	87.1	92.1	88.2	92.7	88.2
% H	5.8	6.1	5.3	5.9	5.4	6.1
% N	1.0	1.4	trace	1.5	trace	1.5
(direct) % O	0.8	4.1	-	-	-	-
% S	not detected	0.6	-	-	-	-
% Carom	80	74	-	74	79	75
% Harom	44	42	53	46	49	45
H/C	.75	.81	.70	0.80	.70	.83

Table 2 : Yield Structure for Asphaltene Pyrolysis.

	Asphaltene A		Asphaltene B	
	mini-bomb	Parr bomb	mini-bomb	Parr bomb
% gas)	28	< 5	35
% pentane sol.) 5 total	15	9	17
% asphaltene	53	3	44	4
% preasphaltene	19	3	34	2
% coke	23	47	8	36

Figure 1

425°C Hydrogenation of Asphaltene B:

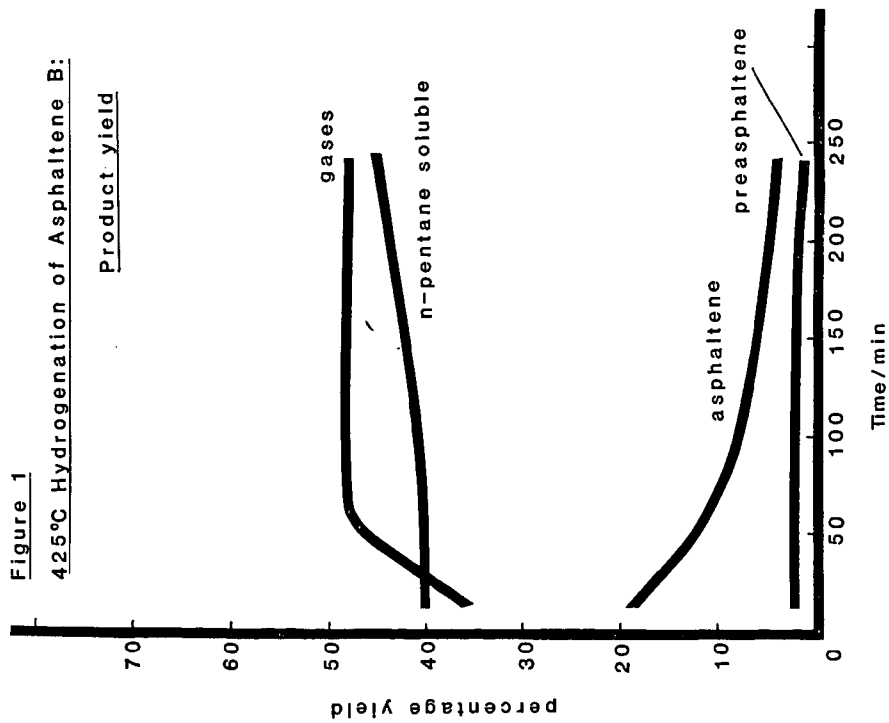


Figure 2

425°C Hydrogenation of Asphaltene A:

